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THE ESTIMATION OF OPALESCENT SILVER CHLORIDE PRECIPITATES.

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In a recent paper upon the nephelometer,[1] a perfected form of this instrument was described and shown to be well fitted for comparing the scanty precipitates usually called opalescences. By the use of prisms the precipitates in two test tubes could be viewed in one field of vision and an accuracy of about 1 per cent was attained in the comparison of nearly equal opalescences. The nephelometer would appear to be a better arrangement than that described by Tswett,[2] because the light strikes the tube sidewise, and one can view the whole tube, instead of looking across the tube through which a pencil of light is passed. Some illustrations of the method of estimating chloride in an unknown solution were given and some general precautions mentioned, but a detailed discussion of the phenomena of opalescent precipitates was reserved for a future paper. During the frequent use of the nephelometer in the revision of the atomic weight of sodium and chlorine,[3] the meth-

[1] Richards and Wells: THIS JOURNAL, 31, 235 (1904).
[2] Z. physik. Chem., 36, 450 (1901).
[3] Richards and Wells: J. Am. Chem. Soc., 27, 484 (1905).

ods of nephelometry were studied and improved until they were sufficiently accurate for the special ends in view. Among the facts which remained to be investigated more thoroughly, however, was the variation of opalescence with time. The present paper contains an account of experiments made upon this subject, as well as upon a great many other points which will widen the range of applicability of nephelometric methods.

Silver chloride is a very suitable salt for studying these questions. Its solubility is small in the ordinary sense, yet large as measured by the nephelometer. The presence of other salts or acids up to concentrations of about N/0.01 does not alter its solubility or at most, only very slightly. In accordance with our present theories of solution the dissolved silver chloride is, on account of the great dilution, completely ionized and there will be, in general, a concentration of silver and a concentration of chloride which will be equal for only one special case. Moreover, it appears to fulfil the demands of the concentration law (mass law) surprisingly well, for a solution of it can be practically freed from chloride by the addition of sufficient ionized silver and from silver by the addition of ionized chlorine.

The difficulty, in previous work, was the selection of the major variables and the control of these so that only one might be varied at a time. This was a hard problem as long as two tubes were compared with each other, for one could not decide whether the observed relative variation was due wholly to the first, partly to the first and second, or wholly to the second tube. The results of this paper would not have been attained if a constant standard of reference had not been found. At first suspensions of chalk were tried,[1] but they proved even more variable than the opalescences. Ground glass, however, appeared to be well adapted to the purpose. Ordinary window glass (plate glass might have been better) was cut into pieces about an inch square and these were ground by fine emery until a series was obtained which ranged from opacity to transparency. Some were ground on both sides. All were covered by black paper having a round hole in the center about 16 mm.

[1] Ostwald-Luther, "Physico-chemische Messungen," p. 248.

in diameter. When such a plate was placed upon the top of the sliding tube in the nephelometer, in a definite and reproducible position, it had exactly the appearance of an opalescent precipitate. The slight color of the window glass only heightened the resemblance. Nearly all the results in this paper, then, were obtained by comparing a single tube of opalescence with a standard glass, and it is evident that the results so obtained are more reliable than the observations published heretofore. Several of the glasses were standardized, after the needful precautions had been learned. For example, one was found by about 20 trials to be equivalent to 15.1 arbitrary units of opalescence, the extremes being 10 and 19. At first sight this does not appear to be at all accurate, but when one reflects that, under improper conditions, the readings might be as high as 45, it appears more satisfactory.

With a constant standard of reference the effect of a great many variations might have been studied. What proved to be major variables proved also to be dependent upon each other. Some of the most obvious influences are the manner of precipitating and stirring the solution. These operations were done as uniformly as possible in all the experiments. Whenever definite, very dilute solutions were prepared, by diluting more concentrated ones, or whenever small quantities of electrolytes were added, the solutions were stirred most thoroughly, and finally allowed to stand for a few minutes to make them still more uniform. During precipitation, also, they were stirred thoroughly and uniformly, usually 20 strokes, with the propeller-shaped platinum stirrers, previously described. More than 20 strokes had no further effect. Failure to stir when precipitation begins results in a noticeable alteration of the intensity of opalescence. Uniform precipitation seems to be hard to attain, but perhaps it might be regulated somewhat by using just the right concentration of precipitant. As regards light, most of these experiments were done in the dim light of a single 16-candle-power light in a dark room. Some were repeated in red light alone, but no difference was detected. When not under direct observation, all tubes stood in a box in absolute darkness. Of course the opalescences darken in day-

light, but no darkening was ever certainly proved to be due to the light of the room in which experiments were performed. Even some weak opalescences exposed to the light of the nephelometer for 2 hours were not darkened perceptibly.

The silver nitrate employed had been sufficiently recrystallized to free it wholly from chloride. The potassium chloride had been purified by precipitation with hydrochloric acid. The nitric acid used had required three wasteful, fractional distillations before it was free from chloride. The potassium nitrate had been evaporated to dryness with the addition of nitric acid until all hydrochloric acid was expelled; it was then recrystallized from water. The sulphuric acid was boiled. Aluminum nitrate was prepared by dissolving clean strips of the metal in the pure nitric acid. Throughout the work great precautions were taken to get rid of contaminating chlorides from the air, the desk and the hands. It is a pleasure to thank Mr. William D. Hutchinson, of Oxford University, for his kind assistance in preparing some of the standard solutions and in making a number of the preliminary observations.

1. Effect of the Medium in which Precipitation Occurs.

When silver chloride is precipitated by mixing fairly concentrated solutions, large curds settle out and very little opalescence is observed. In more dilute solutions, about normal for example, the addition of a silver salt to a chloride leaves a marked opalescence, but, strange to say, the addition of chloride to the silver salt results in a coagulation and, consequently, much less opalescence. Ionized silver, therefore, appears to have marked coagulating power since it is present in excess during precipitation in the latter case. Precipitation from extremely dilute solutions yields a fine state of division or suspension. This coagulates or clarifies slowly upon shaking, much faster in the presence of nitric acid. Similarly, during repeated washings of the precipitate in pure water it tends to go into an emulsion or milky state, which will not clear for days, alone, but usually clarifies by the addition of nitric acid. Now nitric acid has been shown to hasten the development of opalescent precipitates also and one may thus infer that pre-

cipitation and coagulation are very closely related. Indeed, it is impossible to draw any line between the two phenomena—precipitation must be a process of coagulation. The object of the nephelometric experiments was, therefore, to attain this coagulation in a definite and reproducible fashion. It appeared reasonable to suppose that the maximum opalescence which could be attained in any way would most nearly represent the truth. For practical purposes the quickest way to attain that maximum would also be desirable. Hence, it might appear that all experiments should record a study of the speed of precipitation. They should, were it not for the fact that opalescences forming at different rates, in different media, do not, necessarily, attain the same intensity. Very slow precipitations appear, in general, to be swamped by superimposed effects, so that they never attain the maxima which quickly forming opalescences acquire. The variable to be controlled first in nephelometric observations, therefore, is the medium. In order to point out the effect of various media, the maximum opalescences which could be attained, without regard to the time required to attain the maximum, are here stated. Then, under a separate head, will be shown the speeds attained in the best media.

Intense Opalescences.

KCl (N/0.000040) precipitated by $AgNO_3$.

	Intensity of opalescence.
In water	21[1]
N/0.05 HNO_3	29
N/0.05 $Al(NO_3)_3$	29
N/0.025 KNO_3	32

$AgNO_3$ (N/0.000040) precipitated by KCl.

	Opalescence.
Without any electrolyte	21
In N/0.025 $Al(NO_3)_3$	16
In dilute H_2SO_4	28
In N/0.025 HNO_3	30
In N/0.025 KNO_3	31
In $HNO_3 + KNO_3$	26
In $HC_2H_3O_2$	24

[1] These numbers are merely the reciprocals of the heights of opalescence appearing equal to a glass, multiplied by 1000. They indicate intensity of opalescence on an arbitrary scale.

The opalescence in water alone would probably not have been so great if the traces of electrolyte produced by metathesis could have been eliminated. Hence the presence of electrolytes appears advantageous in these intense opalescences.

Weak Opalescences.

KCl (N/o.000007) precipitated by $AgNO_3$.

In the first experiments about a drop of fairly concentrated solutions of various salts was added to each tube. Tubes without any electrolyte attained the greatest opalescence. This was attributed to a possible greater solubility of silver chloride in the solutions containing electrolytes. It may be related to the coagulative power of ionized silver. With only traces of electrolytes, all the tubes behaved similarly. Further experiments might well be made on this case, with special regard to the proper excesses required, according to the results shown later.

$AgNO_3$ (N/o.0000040) precipitated by KCl.

	Opalescence.
In water	14
In N/o.025 KNO_3	20
In N/o.025 $Al(NO_3)_3$	18
In N/o.025 HNO_3	18
In trace of HNO_3	18

A different glass was used for weak opalescences than for intense opalescences. In this case electrolytes appear to be advantageous, as usual.

Experiments were also made with "actual" silver chloride solutions. The phenomena were, in general, similar to the above, except for time effects to be noted later. No better electrolytes than potassium nitrate and nitric acid for intensifying opalescence were found. The quantity to be used depends upon the amount of precipitate; it should be small with slight quantities of precipitate.

It is believed that the excesses used for precipitation in the cases above were sufficient. A full study of that matter had not been made when these results were obtained and hence

less attention was paid to it. Below are given the results bearing upon that particular question.

2. The Excess Required to Produce Maximum Opalescence.

This point has been frequently discussed. Mulder thought that four times the equivalent of soluble salt was required of the precipitant to insure complete precipitation from silver chloride solutions. Stas considered a threefold excess sufficient. Several workers have pointed out that the earlier conclusions varied according to the means used to detect the opalescence.[1] Without regard to theories, experiments were made upon this point.

KCl (N/0.000040) precipitated by $AgNO_3$.

		Intensity of opalescence.
Excess	5 times equivalent of KCl	31, 29 } 30
"	10 " " " "	25, 33 } 29
"	100 " " " "	24
"	1000 " " " "	18

Although any excess of silver nitrate up to 100 times the equivalent of potassium chloride causes no appreciable variation of the opalescence, an excess of 1000 times causes a diminution. This may be due to the great coagulative power of ionized silver, or, more likely, to the formation of a soluble double salt.

$AgNO_3$ (N/0.000040) precipitated by KCl.

			Intensity of opalescence.
Excess	5 times equivalent of $AgNO_3$		23
"	10 " " " "	26, 29, 24, 23, 30 }	26
"	50 " " " "		31
"	200 " " " "		32
"	300 " " " "		22
"	1000 " " " "	28, 27 }	28

[1] Holtsema; Z. physik. Chem., 20, 272 (1896). Richards and Wells: J. Am. Chem. Soc., 27, 483 (1905).

The variation of opalescence with excess is here hardly beyond the limit of error of single observations. Certainly a large excess produces no appreciable diminution of opalescence. The two preceding solutions were very concentrated in comparison with real silver chloride solutions, hence more dilute ones were next investigated.

With very dilute solutions, about N/o.ooooo4 and small excesses, a phenomenon like supersaturation was apparent. Excesses of 8 times usually failed to produce an opalescence, but excesses of 10 times caused a faint opalescence. Here was illustrated the requirement that the solubility product must be exceeded before precipitation can occur. When the solubility product was barely exceeded, opalescence could be made to appear by vigorous stirring. Thus supersaturation does not appear to be limited to soluble salts and there is no reason to suppose that it should be; but it required rather delicate regulation of the concentrations to render it visible in the case of silver chloride. The influence of the medium was very marked. Only results obtained in proper media are given below, the variations for pure water being enormous; in every case where variation with time was observed the maximum is recorded.

KCl (N/o.oooooo40) precipitated by $AgNO_3$.

Excess	25 times equivalent of KCl		Opalescence.
"	75 " " " KNO_3	20	9
"	75 " " " HNO_3	24	24
"	75 " " " both	29	
"	225 " " " KCl	25	30
"	450 " " " "	33	24

Here the result of too small an excess is very marked, but the diminution caused by a large excess is small, if any.

$AgNO_3$ (N/0.0000040) precipitated by KCl.

					Opalescence.
Excess	15-fold	KNO_3	50 min.		14
"	25 "	HNO_3	40 "	17	
"	25 "	KNO_3	50 "	18	20
"	25 "	HNO_3	4 hours	26	
"	50 "	KNO_3	40 min.	26	
"	50 "	HNO_3	40 "	21	24
"	60 "	"	50 "	26	
"	60 "	both	50 "	27	27
"	75 "	"	3 hours		31
"	100 "	KNO_3	40 min.	20	
"	100 "	HNO_3	40 "	30	24
"	100 "	"	2 hours	22	
"	200 "	"	10 min.		18

Notwithstanding the variations which occurred with different media and in the times at which the maxima were observed, a decided regularity is apparent. The maximum opalescence occurs with an excess of about 70 times the equivalent of the ionized silver to be precipitated. If this is more than the theory requires it is probably due to an overcoming of the tendency towards solubility of the silver chloride in the media employed.

The phenomena for medium concentrations undoubtedly lie between the two extremes of N/0.00004 and N/0.000004 studied.

8. The Time Required to Obtain Maximum Opalescence.

The speed of opalescent precipitation is affected by many interrelated variables. For example, it depends upon the excess used, although the influence is not great, providing a proper excess has been used. As one would expect, the greater excess was found to cause a quicker precipitation. Silver nitrate (N/0.000004) was precipitated in two similar solutions containing nitric acid, with opalescence as follows:

Time. Minutes.	Excess 25 times.	Excess 100 times.
10	18	21
50	20	22
540	22	21

The speed is, undoubtedly, affected by temperature. No

experiments were made to illustrate this point, since the tubes which were being compared were usually at the same temperature. The room also remained fairly constant in temperature. This question should receive attention if a method of estimation by standard glasses is perfected, so that corrections could be made for readings taken at different temperatures.

For practical purposes of nephelometry the object is to attain the maximum opalescence in the shortest time possible. The accelerating influence of certain electrolytes had been previously pointed out in a qualitative way.[1] It seemed wise, therefore, to study the specific influence of a number of new electrolytes, following the precipitation in a quantitative way by reference to constant glasses. Below are given some of the results so obtained.

$AgNO_3$ (N/0.000040) precipitated by KCl (10-fold excess.)

Time.	Without addition of any salt.	In N/0.025 KNO_3 (trace of HNO_3).	KNO_3 + HNO_3.	HNO_3.	Trace HNO_3.	$Al(NO_3)_3$ (trace HNO_3).	Dilute H_2SO_4.	Trace H_2SO_4.	$C_2H_2O_4$.
	Opalescences.								
1 min.	8	25	16	15	11	14	9	8	7
15 "	9	31	26	30	13	16	.	.	10
30 "	10	29	23	29	14	15	28	13	.
80 "	14	28	20	28	14	16	27	19	21
4 hrs.	20	24	21	26	17	16	26	24	23
14 "	21	18	18	24	16	16	23	.	24

It will be noticed that the tube containing potassium nitrate attains maximum opalescence in 15 or 20 minutes. Next in order of speed follow the tubes containing nitric acid, potassium nitrate plus nitric acid, and sulphuric acid. The tube without any electrolyte except that added to precipitate or that produced by metathesis was still increasing slowly at the end of 14 hours. The results were not always so without electrolytes, however, as was shown when considering the medium under the head, weak opalescences.

Such readings, extending over many hours, were made with

[1] Richards and Wells: J. Am. Chem. Soc., 27, 486 (1905).

intense, medium and weak opalescences when precipitated by the addition of silver nitrate to potassium chloride, potassium chloride to silver nitrate and each of these salts to actual solutions of silver chloride, in the presence of the various electrolytes above mentioned, about 400 observations in all. The publication of these readings would require many pages. Since many of them turned out to be mere repetitions it seems wiser to state only the general conclusions.

In general, the substances which aid in producing maximum opalescence also hasten the speed of its formation. Hence, the behavior in water alone was exceptional in every case, except that of the very weakest opalescences. No better accelerators than the "strong electrolytes," salts and the mineral acids, were found. The time of maximum opalescence with good accelerators present varied for the different cases, roughly as follows:

Intense opalescences (about N/0.00005).

	Time of maximum. Minutes.
$AgNO_3$ added to KCl	4
" " " AgCl	20
KCl " " $AgNO_3$	30
" " " AgCl	20

Medium opalescences (about N/0.00002).

	Time of maximum. Minutes.
$AgNO_3$ added to KCl	10
" " " AgCl	25
KCl " " $AgNO_3$	25
" " " AgCl	25

Weak opalescences (about N/0.000005).

	Time of maximum. Minutes.
$AgNO_3$ added to KCl	20
" " " AgCl	30
KCl " " $AgNO_3$	30
" " " AgCl	30

In practice it was so difficult to control all but one variable that the results above have a relative rather than an absolute significance. Particularly, too much significance must not be

attached to the times, 30 minutes and over, for the opalescence had, in those cases, become so stable that it usually varied only slightly for 3 or 4 hours further, and the exact maximum fell now at one time, now at another. On this account, if the most exact results are desired, observations should always continue until opalescence begins to fade. Only in this way can one be absolutely certain that the maximum has been attained. That these insignificant variations were due to the state of the water or temperature is rendered probable by the fact that, when the maximum was late in its attainment in one case it was late in the other tubes that day.

Perhaps the most striking fact in the results is that "actual" silver chloride solutions attain their maximum so much more uniformly than chlorides or silver salts precipitated by the opposite ion. These facts bear upon atomic weight work. In the equal opalescence method, with chloride, the time of observation need not be extended beyond an hour, although no error would be introduced by so doing. In determining chloride in a silver chloride solution, however, by nephelometric methods, this point would have to be considered. The proper procedure would be to precipitate the unknown silver chloride solution, allowing it to develop for 16 minutes, then to precipitate the standard solution and make the comparison at the end of the next 4 minutes. The time would be somewhat differently adjusted if silver were being determined. But the use of a glass as a standard of reference would be the best way of all.

A small correction may now be made for this error in determining the atomic weight of sodium. Since the unknown opalescence attained its maximum after the known had begun to fade, too much standard solution was used to match, finally, the unknown opalescence; hence the soluble chloride recorded was too great. The error so committed might have amounted to 20 per cent in the solubility, therefore about 0.002 per cent in a usual determination, hence 0.001 unit in the atomic weight of sodium. The result attained by the gravimetric method, 23.006 (if Ag = 107.93), would become 23.007 with this correction, therefore, but the final average with the result of the equal opalescence method, 23.009, would still remain 23.008.

It is also now very clear why, in the earlier work with the nephelometer, the ratio of two tubes occasionally changed enormously with time,[1] for the standard was increasing in intensity, the unknown solution decreasing. This is shown by the following example:

Time.	Ratio of opalescences.
5 min.	3.20
15 "	2.76
30 "	2.20
60 "	1.59
2.5 hours	1.19
7 "	1.08
15 "	0.99

It also becomes interesting to speculate as to the causes of the ever shifting opalescences. It is evident that a given number of small, separate, visible particles will cause a greater opalescence than the same number collected into an aggregation, for the reflecting surface exposed will be greater. But if it be assumed that some of the single particles are too small to reflect light at all, that would not be true. As the latter assumption is a likely one, the development of opalescence is probably due to aggregation, and precipitation is only the point where the aggregations first attain the limit of visibility. The aggregation may be hastened initially by the presence of electrolytes. The action has been variously explained; Whetham shows agreement between the facts and the theory that a certain number of electrostatic charges must be brought within reach of a colloidal group.[2] Hence, he assumes that coagulation occurs in consequence of a change in the surface energy of the colloids, due to the presence of the electrostatic charge. Quincke explains the phenomena solely by surface tension changes. It seems reasonable to suppose that aggregation could only be expected to occur rapidly while the particles are small and their kinetic motion or diffusion is rapid. As aggregations become larger the process will become slower, until a point is reached where all aggregations have attained the

[1] J. Am. Chem. Soc., 27, 484. Many results attained in the earlier work appeared so anomalous that they were never published.

[2] "A Treatise on the Theory of Solution," p. 396 (1902).

limit of visibility and the exposed surface, and therefore the opalescence, begins to decrease, owing to further aggregation. The decrease is less dependent upon the medium than is the initial formation of opalescence. Moreover, a small part of the decrease is due to settling of the particles under the influence of gravity.

The above suppositions are very closely related to the present theories of colloids, and the peculiar behavior of silver chloride has previously been ascribed to its colloidal condition.[1] But Picton and Linder have pointed out that there is probably no difference in kind between a colloid and a crystalloid.[2] This is made especially clear by Beckhold in a paper upon the agglutination of bacteria.[3] He points out that is a continuous transition from crystalloids in the first place to those bodies, partly colloidal, which aggregate in solution so as to produce high molecular weight, then to the real colloids, which look like solutions but are really suspensions and, finally, to the visible suspensions. Many colloids are coagulated by the addition of univalent, bivalent and trivalent salts with the relative speeds, 1 : 35 : 1023.[4] The action of aluminum nitrate was tried for the purpose of seeing if silver chloride belongs to this class. Since aluminum nitrate had no unusual effect, two possibilities remained. Either silver chloride is not a colloid, or else it is one which moves with an electric current and hence, according to Hardy,[5] one would expect only anions to affect its coagulation. Without knowing about its movement in an electric field, coagulation in the presence of sulphates was tried. These also failed to cause unusual speed of coagulation. Hence, there remained only one argument in favor of the colloid theory, the occasional color of the opalescences. This, however, can be accounted for by strictly physical conceptions. The only tints appearing were a pale blue or a faint reddish-brown; now Lord Rayleigh has shown that when the size of

[1] Richards and Wells: J. Am. Chem. Soc., 27, 484.
[2] J. Chem. Soc., 61, 148 (1892).
[3] Z. physik. Chem., 48, 385 (1904).
[4] Schulze: J. prakt. Chem., 25, 431 (1882).
[5] P. Roy. Soc., 66, 110 (1900).

reflecting particles approaches the wave length of light they begin to cease reflecting; but the short blue waves are reflected by particles small enough to transmit the red waves. It seems probable, then, that opalescences occasionally appear blue for the same reason that the sky does,—the smallness of the reflecting particles. Similarly, the red tints would be accounted for by transmitted light which has lost its blue component by partial dispersion, though these were not so frequently observed as the blue tints.

It is also interesting to notice that many of the phenomena studied in this paper have a direct bearing upon photography. During the ripening of plates the change of powdery to granular silver chloride takes place. Eder records that unripe emulsions show the red and blue tints by transmitted light.[1] According to Liesegang the presence of potassium bromide in developers increases the size of the granules of silver,[2] but this is just what would be expected in accordance with the results of the nephelometer.

4. Proper Treatment for Estimating Various Opalescences.

In order to save the time of those attempting nephelometry, the precautions for several typical cases are here collected:

Intense Opalescences (N/0.00005):

Silver nitrate added to potassium chloride: Add nitric acid or potassium nitrate. Use 8-fold excess. Read in 4 minutes.

Silver nitrate added to silver chloride already containing potassium nitrate. Read in 20 minutes.

Potassium chloride added to silver nitrate: Add electrolyte. Use 50-fold excess. Read in 30 minutes.

Potassium chloride added to silver chloride, already containing potassium nitrate. Read in 20 minutes.

Weak Opalescences (N/0.000005):

Silver nitrate added to potassium chloride: Add electrolyte. Use 100-fold excess. Read in 20 minutes.

Silver nitrate added to silver chloride, already containing electrolyte. Read in 30 minutes.

[1] "Photographie," 9, 66 (1902).

[2] *Loc. cit.*, p. 102.

Potassium chloride added to silver nitrate: Add electrolyte. Use 70-fold excess. Read in 30 minutes.

Potassium chloride added to silver chloride, already containing electrolyte. Read in 30 minutes.

In general, therefore, the object is to make the standard tubes as nearly like the unknown as possible, or, if standard glasses are being used, to attain the maximum.

The question naturally arises whether the forced maxima are really as uniform as less intense opalescences attained after repose. A considerable weight of confirmatory evidence, which will appear shortly in another paper, shows, conclusively, that the maxima are the best measures of the concentration. Moreover, electrolytes must be present in some solutions and uniformity, therefore, demands that they be present in all. It is very likely that, occasionally, an extreme maximum will be produced, just as too weak opalescences may occur ; hence the average of several observations will approach nearer the truth than only one or two.

Summary.

1. The chief sources of error in previous nephelometric work are pointed out.

2. The use of ground glass standards of reference proved advantageous in studying the variation of opalescent precipitates with time.

3. For every concentration a suitable medium and excess of precipitant is required.

4. Electrolytes both augment the maximum opalescence to be precipitated from a solution and hasten its deposition.

5. The bearing of these facts upon other fields is pointed out.

6. Directions for procedure are given for several special cases of nephelometry.

CHEMICAL LABORATORIES, HARVARD COLLEGE AND UNIVERSITY OF PENNSYLVANIA, 1905.

Contribution from the Kent Chemical Laboratory of the University of Chicago.

ON THE BEHAVIOR OF BENZOYL CARBINOL TOWARDS ALKALIES AND OXIDIZING AGENTS.

By Wm. Lloyd Evans.

Zincke and his students were the first to study the behavior of benzoyl carbinol towards oxidizing agents.[1] They found that it gives, according to the oxidizing agent used, varying proportions of mandelic, benzoylformic, benzoic and carbonic acids. The most notable of their experiments was the action of copper and sodium hydroxides on benzoyl carbinol and acetolacetate, *r*-mandelic and *r*-lactic acids, respectively, being the chief reaction products obtained. Zincke suggested[2] that in this reaction the benzoyl carbinol might first be resolved into benzaldehyde and formaldehyde and that these products might subsequently combine to give *r*-mandelic aldehyde, whose conversion to the corresponding acid, in the presence of the oxidizing agent, would then be readily understood. He also presented the view that the aldehyde of benzoyl carbinol might first be formed by direct oxidation of the primary alcohol group present in benzoyl carbinol and that the resulting benzoylformaldehyde might be converted to mandelic acid by intramolecular oxidation and reduction,[3]

$$O : C(C_6H_5)CH : O + H_2O \rightarrow C_6H_5CH(OH)COOH.$$

Kling, in his recently published statement,[4] divides the action of oxidizing agents into three categories, according to the relative amount of lactic, acetic and carbonic acids obtained from the analogous acetyl carbinol.

It is clearly evident from the work of Nef[5] that mandelic and lactic aldehydes cannot be isolated as such, but are transformed spontaneously into the isomeric benzoyl and acetyl

[1] Ber. d. chem. Ges., 13, 635. Ann. Chem. (Liebig), 216, 311.
[2] *Ibid.*, 216, 314.
[3] Cf. V. Meyer: Ber. d. chem. Ges., 13, 2344.
[4] Bull. Soc. Chim., [3], 33-34, 1,49. Compt. rend., 139, 740-742.
[5] Ann. Chem. (Liebig), 335, 247-279.

carbinols, which are not tautomeric compounds. Furthermore, the conversion of benzoyl or acetyl carbinol into *r*-mandelic or *r*-lactic aldehyde by dissociation and subsequent addition, as assumed by Zincke (see above) is excluded, as Nef has shown that an equimolecular mixture of formaldehyde and acetaldehyde gives absolutely no *r*-lactic acid in the presence of cupric hydroxide and sodium hydroxide. Nef, therefore, came to the conclusion that benzoyl- and acetylformaldehydes, respectively, must first be formed in the reaction under discussion and that the conversion of the resulting aldehydes into lactic and mandelic acids is due to a benzilic acid rearrangement. As is well known, almost all orthodicarbonyl compounds,

$$\begin{matrix} XC:O \\ | \\ YC:O \end{matrix}$$

whether in open chains or closed cycles, undergo such a rearrangement or conversion, by absorption of 1 molecule of water, into α-hydroxy acids,

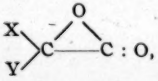
$$XYC(OH)CQOH.$$

In some cases, as with hexaketomethylene and diketosuccinic acid, this rearrangement takes place quantitatively in dilute aqueous solution; in most instances it requires the presence of more or less concentrated aqueous caustic alkalies, or at times even solid potassium hydroxide at higher temperatures. Nef[1] has presented the following interpretation of this remarkable rearrangement: The orthodicarbonyl compound $\begin{matrix} XC:O \\ | \\ YC:O \end{matrix}$ dissociates into $XYC:O$ and $\diagdown C:O$; the products of dissociation, in their active molecular form

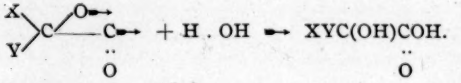
$$XYC\begin{matrix}—O \\ | \\ | \end{matrix} + \diagup C:O,$$

unite to form the addition product,

[1] Ann. Chem. (Liebig), **335**, 272-273.



which then, by hydrolysis, gives the α-hydroxyacid



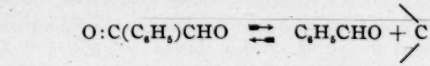
At the suggestion and under the supervision of Professor J. U. Nef I have taken up a careful and exhaustive quantitative study of the behavior of benzoyl carbinol towards oxidizing agents under the most varied conditions. The work of Nef during the past 10 years on the monoatomic alcohols, aldehydes and fatty acids, as well as on glycols, glycerols and sugars, has shown that it is possible to follow, rigidly, by experiment, the course taken by many apparently complicated oxidation processes. The problem in the benzoyl carbinol series seemed especially susceptible of experimental treatment; first, because the possible acid oxidation products, benzoic, *r*-mandelic and benzoylformic acids were all well-known, crystalline compounds, and quantitative methods for their sharp separation could easily be worked out; second, because the first possible oxidation product of benzoyl carbinol, namely, benzoylformaldehyde was known, having been discovered by v. Pechmann,[1] and its behavior on oxidation could, consequently, be carefully investigated. These expectations were in every way realized; my experiments prove, in a most rigid manner, the correctness of all the conclusions reached by Nef, as briefly presented above. Of special importance is the behavior of benzoylformaldehyde under various conditions. This substance is converted quantitatively into *r*-mandelic acid, very rapidly at ordinary temperatures, by all soluble caustic alkalies, even in most dilute aqueous solutions, and also by aqueous copper acetate solutions at 70°–100°. The behavior of benzoylformaldehyde towards various oxidizing agents alone and in the presence of dilute caustic alkalies

[1] Ber. d. chem. Ges., **30**, 2904; **22**, 2556.

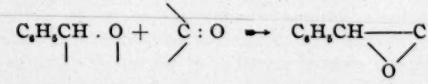
proves, in a most convincing manner, that this substance, in the process of transformation into *r*-mandelic acid by a benzilic acid rearrangement, must first be dissociated into benzaldehyde and carbonic oxide, as assumed by Nef. The facts are these: A. Benzoylformaldehyde gives, with freshly precipitated mercuric or silver oxides, alone or in the presence of caustic alkalies, benzoic and carbonic acids only; separate experiments with mandelic and benzoylformic acids and the oxides named prove that this oxidation cannot possibly have taken place with the intermediate formation of these acids. B. Benzoylformaldehyde, with cupric oxide and caustic alkalies, as well as with potassium ferricyanide and potassium hydroxide, gives, practically, *r*-mandelic acid *only*. C. Benzoylformaldehyde, with aqueous potassium permanganate, in the cold, gives, practically, only benzoic acid; under the same conditions, but in the presence of caustic alkalies, about equal amounts of benzoylformic, benzoic and carbonic acids are formed. It is, moreover, certain that the benzoylformic acid is formed from *r*-mandelic acid obtained by a benzilic acid rearrangement of the aldehyde, and not through a direct oxidation of the aldehyde, and its proportion undoubtedly varies with the concentration of the alkali used.

The only possible interpretation of the results, A, B and C, is the following:

I. Benzoylformaldehyde is partially dissociated into carbonic oxide and benzaldehyde,



II. The relative rate of transformation of the products of dissociation I into *r*-mandelic acid,



and the relative rate of oxidation of these dissociation products into benzoic and carbonic acids varies in cases A, B and C, re-

spectively. In other words, benzaldehyde and carbonic oxide, reacting, as is known, very readily with the oxides of mercury and silver, are entirely oxidized in the presence of these reagents before they can unite to form *r*-mandelic acid (case A).

In the presence of alkalies and cupric hydroxide or potassium ferricyanide, on the other hand, since these are very mild oxidizing agents, *only* a benzilic acid rearrangement takes place, *i. e.*, the formation of *r*-mandelic acid (case B). If potassium permanganate, without alkalies, is used on benzoylformaldehyde no rearrangement to *r*-mandelic acid occurs, but with alkalies present (case C) about 50 per cent of oxidation of its dissociation products and 50 per cent of transformation to *r*-mandelic acid takes place. This is not surprising, since in oxidation by potassium permanganate,

$$2KMnO_4 + H_2O \rightarrow 2KOH + 2MnO_2 + 3O,$$

the amount of alkali set free in the reaction is only sufficient to form salts with the benzoic and carbonic acids which are formed; no experiments were carried out to determine the velocity of the transformation of benzoylformaldehyde into *r*-mandelic acid with varying concentration of the alkali.

These results, therefore, establish experimentally the correctness of Nef's interpretation of the benzilic acid rearrangement; there are, furthermore, numerous observations in the literature which prove that many ortho or 1,2-dicarbonyl compounds undergo dissociation into carbonic oxide and a monocarbonyl derivative at comparatively low temperatures, and this must also be considered as evidence pointing to the same conclusion. Thus benzil and hydroxyoxalacetic ester readily decompose, at 250°–300°, into carbonic oxide, benzophenone and hydroxymalonic ester, respectively.

EXPERIMENTAL PART.

Preparation of Benzoyl Carbinol.—Owing to the extreme sensitiveness of benzoyl carbinol, especially towards alkaline reagents, the methods heretofore used in its preparation[1] were found to give very unsatisfactory yields; the same is true

[1] Graebe: Ber. d. chem. Ges., 4, 34. Hunnius: *Ibid.*, 10, 2910. O. Fischer and Busch: *Ibid.*, 24, 2680. Zincke: Ann. Chem. (Liebig), 216, 306.

when bromacetophenone or α-bromphenylacetaldehyde are digested with potassium formate and methyl alcohol, methods which give acetol quantitatively with the corresponding derivatives in the fatty series.[1]

The hydrolysis of benzoyl carbinol acetate by means of 17 parts of boiling water, for 12 hours, was finally found to be the best means of preparing this substance; bromacetophenone was made from 75 grams of acetophenone, according to the directions of Möhlan[2] and the crude oil, 124 grams, precipitated by water, was converted into the acetate by digesting for 3 hours, under a reversed condenser, at 125°–130°, with 310 grams of glacial acetic acid and 100 grams of fused sodium acetate. One hundred grams of crude acetate were thus obtained by addition of water, extraction with ether and removal of the acetic acid by washing with sodium carbonate solution; on distillation under 10–15 mm., 5.3 grams of this boiled below 130° and the remainder, 89 grams, 80 per cent of the theoretical, at 145°–155°, leaving 5 grams of tar in the distilling flask. On hydrolysis of the main fraction of the acetate, as mentioned above, 49 grams of pure benzoyl carbinol, crystallized from ether-ligroin and melting at 85°–86°, were obtained, besides 3.5 grams of tar, insoluble in boiling water. Benzoyl carbinol boils, according to the observations of Nef, without the slightest decomposition, at 118°–120° (11 mm.); on distilling 10 grams of it, under 10 mm. pressure, through a combustion tube filled with pumice, kept at 400°–440°, in a 28 burner furnace, 7 grams of carbinol were recovered unchanged (time, 10–15 minutes); on repeating the experiment, but raising the temperature to 580°–600°, much decomposition with gas evolution took place. The liquid decomposition products, 2.50 grams, were proved to contain benzene and benzaldehyde, which was identified as phenylhydrazone; 0.80 gram, m. p. 158°, was obtained. A strong odor of formaldehyde was noticed in the apparatus. This proves that benzoyl carbinol dissociates, by heat, in a manner analogous to acetol,[3] into benzaldehyde and formaldehyde,

[1] Ann. Chem. (Liebig), 335, 260, 265.
[2] Ber. d. chem. Ges., 15, 2464.
[3] Nef: Ann. Chem. (Liebig), 335, 250.

$$C_6H_5COCH_2OH \rightarrow C_6H_5CHO + H_2C:O.$$

Action of Benzoyl Carbinol on Copper Salts.—In the cold the first stage in the action of aqueous copper acetate and copper sulphate, respectively, on benzoyl carbinol is the conversion into benzoylformaldehyde, as was proved by special experiments; in the former case cuprous oxide is formed and in the latter metallic copper is deposited. It is extremely probable that, in both cases, there is first an intermediate formation of cupric benzoyl carbinol,[1] and this, like all salts of primary and secondary alcohols, has a much lower dissociation point than the corresponding alcohol; consequently the following reaction takes place:

$$(C_6H_5COCH_2O)_2Cu + 2H_2O \rightarrow$$

$$2C_6H_5COCH\diagup\diagdown + Cu(OH)_2 + 2H.OH \rightarrow$$

$$2C_6H_5COCH(OH)_2 + 2H + Cu(OH)_2.$$

The atomic hydrogen thus formed then reduces the cupric salt present either to metallic copper or to the cuprous state.

Benzoyl Carbinol and Cupric Acetate.—Five grams of benzoy carbinol, dissolved in 120 cc. of warm water, were added to a solution of 22 grams (3 mols.) of crystallized copper acetate, in 350 cc. of water; the temperature of the resulting solution was at first 35° and cuprous oxide began to separate out almost immediately. The mixture was allowed to attain room temperature and was then left standing for 14 days. The precipitate of cuprous oxide was found to weigh 3.5 grams and the aqueous filtrate was extracted 18 times with ether. The oily residue, obtained on evaporating the moist ether extracts, was freed from acetic and other acids by digestion with water and 4 grams of calcium carbonate; the aqueous filtrate, again extracted thoroughly with ether, yielded, on evaporation of the moist ether and on drying over sulphuric acid *in vacuo*, 3.9 grams of a neutral, crystalline, pungent smelling substance,

[1] Nef: Ann. Chem. (Liebig), **335**, 275.

melting at 70° ; on crystallizing from water it melted at 78° and remained unchanged when mixed with an equal amount of v. Pechmann's[1] benzoylformaldehyde monohydrate. The identity of the product obtained with benzoylformaldehyde was furthermore established by the following tests :

a. One-half gram, dissolved in 40 cc. of water, was treated with 0.2 gram of powdered calcium hydroxide, in the cold ; the solution turned yellow at once and after standing 12 hours gave, on acidifying with hydrochloric acid and thorough extraction with ether, 0.5 gram of *r*-mandelic acid, m. p. 118°.5.

b. One-half gram of the aldehyde, dissolved in 4 cc. of 50 per cent alcohol gave, on addition of 0.05 gram of potassium cyanide and subsequent addition of water, 0.3 gram of the yellow benzoin derivative of benzoylformaldehyde,

$$C_6H_5COCH(OH)COCOC_6H_5,$$

first obtained by Söderbaum ;[2] the melting-point of this product was found to be 180°, with previous darkening at 176°, whereas Söderbaum found 170°.

c. The benzoylformaldehyde obtained on treatment with Fehling's solution does not give the slightest reduction to cuprous oxide. This is in harmony with v. Pechmann's observation ; with silver oxide, on the other hand, a reduction to metallic silver takes place at higher temperatures (see below). Since pure benzoylformaldehyde and benzil are without action on Fehling's solution, it is very probable that other pure orthodicarbonyl compounds, such as glyoxal, acetylformaldehyde and diketosuccinic acid, must behave in a similar manner towards this reagent, as it must simply transform the compounds, by a benzilic acid rearrangement, into the corresponding α-hydroxy acids. I therefore conclude that acetylformaldehyde, which is the perfect analogue of benzoylformaldehyde in the fatty series, and which has recently been isolated by Harries and Turk,[3] must have contained some impurity, as the product obtained by them is described as reducing Fehling's solution. Finally, it should be mentioned that, in addition to

[1] Ber. d. chem. Ges., **22**, 2557.
[2] *Ibid.*, **24**, 1381, 3038.
[3] *Ibid.*, **38**, 1630.

the main neutral reaction product obtained in the experiment above described, the aqueous solutions containing lime salts of acids gave, when worked up by the method described below, 0.15 gram of benzoic acid, m. p. 121°, and 0.35 gram of mandelic acid, m. p. 118°, but no trace of benzoylformic acid.

Benzoyl Carbinol and Copper Sulphate.—No action was noticed on mixing cold, aqueous solutions of 5 grams of benzoyl carbinol and 18.2 grams (2 mols.) of crystallized copper sulphate, the total volume being 400 cc., but on allowing the mixture to stand outdoors in the sunlight, for 2.5 months, the solution had changed to dark green, the action being accompanied by a deposition of copper. It was now warmed for 6 hours at 50°–60°, finally, for a short time, at 100°, and then filtered from the copper, 1.10 grams. The aqueous filtrate was extracted with ether and the reaction products separated into acid and neutral portions, as mentioned above, by powdered calcium carbonate. There were obtained, as reaction products, 2.7 grams of benzoylformaldehyde monohydrate, melting at 78°, containing traces of unchanged carbinol, and 0.5 gram of *r*-mandelic acid, melting at 118°.5, besides 0.25 gram of benzoic acid.

The quantitative separation and determination of the relative amounts of benzoic, benzoylformic and *r*-mandelic acids formed in the various cases was always carried out as follows: The acid mixture was first distilled with steam, which carried over only benzoic acid. The non-volatile portion was then treated with phenylhydrazine, dissolved in an equal volume of 50 per cent acetic acid and, after 24 hours' standing, benzoylformic acid phenylhydrazone separated out completely. It was purified by dissolving in dilute sodium carbonate solution, reprecipitating by dilute sulphuric acid and crystallizing from hot benzene.[1] From this the amount of keto-acid present could be determined by calculation. The aqueous filtrate from the phenylhydrazone, containing only *r*-mandelic acid, was worked up for this acid by thorough extraction with ether and subsequent washing with dilute sulphuric acid. The residue, after the evaporation of the ether, was heated at 100° (25–30 mm.)

[1] Cf. Nef: Ann. Chem. (Liebig), **280**, 295.

in order to remove the acetic acid. The *r*-mandelic acid was finally crystallized from a mixture of ether and ligroin (70°–80°).

The Behavior of Benzoylformaldehyde towards Copper Salts at 100°.—The most striking property of benzoylformaldehyde is its transformation into *r*-mandelic acid, which takes place very rapidly with all aqueous caustic alkalies, even in the cold and in most dilute solutions. This was first observed by v. Pechmann and Söderbaum[1] and has been repeatedly confirmed by me.

The conversion of the aldehyde into *r*-mandelic acid also takes place by heating with aqueous solutions of various copper salts, as is proved by what follows: Two grams of benzoylformaldehyde hydrate and 2.97 grams of crystallized copper acetate, dissolved in 70 cc. of water, were boiled for 1 hour. There was a gradual separation of insoluble greyish-white crystalline copper mandelate.[2] The precipitate was dissolved in dilute hydrochloric acid and, on extracting well with ether as described, 1.7 grams of pure *r*-mandelic acid, m. p. 118°.5, were obtained. A special experiment with a solution of 2 grams of benzoylformaldehyde and 8.10 grams of copper acetate, in 225 cc. of water, proved that, on standing 3 days at ordinary temperatures, no transformation into *r*-mandelic acid had taken place. On extracting the solution 18 times with ether and heating with calcium carbonate in the usual manner, 1.44 grams of aldehyde were recovered unchanged. A solution of 1 gram of benzoylformaldehyde hydrate and 1.25 grams of crystallized copper sulphate, in 100 cc. of water, was heated at 130°, for 7 hours; 0.55 gram of bluish-white copper mandelate precipitated, from which 0.30 gram of the pure acid was obtained. The aqueous filtrate yielded 0.5 gram of oily residue, which was proved to be mainly unchanged aldehyde by conversion into 0.40 gram of pure *r*-mandelic acid, by means of sodium hydroxide.

Special experiments with an aqueous solution of *r*-mandelic acid, containing molecular quantities of copper acetate or cop-

[1] *Loc. cit.*

[2] Ann. Chem. (Liebig), 18, 320.

per sulphate, proved that in both cases there is practically complete precipitation of copper mandelate on warming on a boiling water-bath, acetic and sulphuric acids, respectively, being thus set free.

Benzoyl Carbinol and Copper Salts at 100°.—In view of the results just presented, the following experiment with benzoyl carbinol and aqueous copper acetate needs no further elucidation. A solution of 5 grams of benzoyl carbinol and 22 grams of crystallized copper acetate (3 mols.) dissolved in 425 cc. of water, was heated, after standing 12 hours, first at 50°–60° and finally for 3 hours at 100°. The precipitate, which at first consisted only of cuprous oxide, gradually became covered with cupric mandelate. The total weight was 10 grams and from this, by treatment with dilute hydrochloric acid and extraction with ether, 4 grams of pure mandelic acid were obtained. The aqueous filtrate, acidified with dilute sulphuric acid and extracted with ether, etc., gave 0.10 gram of benzoic acid, melting at 121°, 0.20 gram of *r*-mandelic acid, melting at 118°.5, and a trace of benzoylformic acid.

Benzoyl Carbinol and Cupric and Sodium Hydroxides.—Benzoyl carbinol and acetol, respectively, reduce Fehling's solution very rapidly in the cold. The quantity of oxygen used in the oxidation of the acetol has been determined by W. H. Perkin, Jr.,[1] and others, and found to be 1 atom. It is practically certain, from Zincke's experiments with acetol and benzoyl carbinol,[2] and from the following one with benzoyl carbinol that *r*-lactic and *r*-mandelic acids, respectively, are formed in this oxidation process. Furthermore, the oxidation proceeds through an intermediate formation of acylformaldehyde, which then, in the presence of the strong caustic alkali, immediately undergoes a benzilic acid rearrangement.

The benzoyl carbinol undoubtedly forms a sodium or potassium salt with the caustic alkali present,[3] which, having a low

[1] J. Chem. Soc., **59**, 788.
[2] *Loc. cit.* Cf. Nef: Ann. Chem. (Liebig), **335**, 273.
[3] Nef: *Loc. cit.*

dissociation point, is relatively much dissociated at ordinary temperatures into benzoyl methylene,

$$C_6H_5COCH_2ONa \rightleftharpoons C_6H_5COCH\!\!\diagup\!\!\diagdown + HONa;$$

the latter then takes up the hydroxyl ions present, giving benzoylformaldehyde hydrate and the atomic hydrogen or kation thus set free reduces the bivalent copper to cuprous oxide. Since bromacetophenone is also partially dissociated into benzoyl methylene and hydrogen bromide,

$$C_6H_5COCH_2Br \rightleftharpoons C_6H_5COCH\!\!\diagup\!\!\diagdown + HBr,$$

at ordinary temperatures, it is to be expected that this substance must give, with Fehling's solution as well as with sodium and cupric hydroxides, exactly the same results as benzoyl carbinol; this is proved by what follows: Five grams of benzoyl carbinol, in 310 cc. of water, were added to a solution of 18.10 grams (2 mols.) of crystallized copper sulphate, in 90 cc. of water. On the addition of 8 grams of sodium hydroxide (5 mols.), dissolved in 24 cc. of water, reduction to cuprous oxide took place at once, in the cold. The mixture was finally warmed for 15 minutes on a water-bath, filtered and the yellow filtrate evaporated to dryness under 15–20 mm. pressure (bath 100°). On acidifying with hydrochloric acid and extracting 7 times with ether, a total of 5.15 grams of reaction product was obtained. This gave, by working up in the usual manner, 3.70 grams of *r*-mandelic acid, melting at 118°; 0.10 gram of pure benzoic acid and 0.25 gram of benzoylformic acid (from 0.40 gram of the hydrazone).

Bromacetophenone and Cupric and Sodium Hydroxides.—Five grams of bromacetophenone, suspended in a solution of 12.5 grams (2 mols.) of crystallized copper sulphate, in 300 cc. of water, were treated with 10 grams of sodium hydroxide (5 mols.) in 100 cc. of water. On shaking violently, reduction to cuprous oxide took place at once and, after standing in the cold for 24 hours and then working up as in the previous case,

I obtained 2.30 grams of pure mandelic acid, besides 1 gram of unchanged bromacetophenone. When this experiment was repeated at 100°, for 8 hours, only 2.40 grams of crude reaction products were extracted by ether, and from this I obtained 0.50 gram of benzoic acid, 0.41 gram of mandelic acid and 0.25 gram of benzoylformic acid.

Benzoyl Carbinol, Potassium Hydroxide and Potassium Ferricyanide.—Five grams of benzoyl carbinol, dissolved in 300 cc. of water, were added to a mixture of 60.4 grams of potassium ferricyanide and 10.4 grams of potassium hydroxide, in 400 cc. of water, the resulting temperature being 38°. After standing 12 hours, the mixture was worked up by acidifying with dilute sulphuric acid and extracting 6 times with ether. Three and seven-tenths grams of pure mandelic acid, besides 0.30 gram of benzoic acid, were finally obtained. A special experiment with 0.5 gram of benzoylformaldehyde hydrate, dissolved in 25 cc. of water and 18 cc. of a solution containing 3.25 grams of potassium ferricyanide and 0.85 gram of potassium hydroxide, after standing 4 hours in the cold, gave 0.40 gram = 80 per cent of the theoretical amount of pure mandelic acid. It is obvious, therefore, without further comment, that the reactions with benzoyl carbinol and alkaline copper and ferricyanide solutions proceed in a perfectly analogous manner. Finally, a special experiment with 2 grams of mandelic acid, 10.80 grams of potassium ferricyanide, 3 grams of potassium hydroxide, dissolved in 150 cc. of water, proved that, after 24 hours' standing in the cold, no oxidation of the acid had taken place, as 1.80 grams were recovered unchanged by working up in the usual manner.

Acetophenone, Potassium Ferricyanide and Potassium Hydroxide.—According to the literature,[1] acetophenone gives benzoylformic and benzoic acids, by oxidation with the reagents just named. These observations were confirmed and it was proved with special care that no trace of *r*-mandelic acid is formed in this case. This shows that the oxidation reactions with acetophenone cannot possibly proceed in a manner analogous to those of benzoyl carbinol and bromacetophenone; there was,

[1] Buchka and Irish: Ber. d. chem. Ges., 20, 389.

a priori, a possibility of this. Five grams of acetophenone were added to a solution containing 68 grams of potassium ferricyanide (2.5 atoms of oxygen), 16 grams of potassium hydroxide and 800 cc. of water. The reaction sets in at once, in the cold; after 36 hours' standing and filtering from a small amount of yellow, flocculent precipitate, the solution was acidified with dilute sulphuric acid and worked up for acids by extracting with ether, etc. I obtained 1.05 grams of benzoylformic acid, 0.20 gram of benzoic acid, 0.70 gram of tar, but no mandelic acid.

Benzoyl Carbinol and Potassium Permanganate.—A solution of 5 grams of benzoyl carbinol, in 120 cc. of warm water, was slowly added to 7.40 grams of potassium permanganate (3 mols.) dissolved in 300 cc. of water, which was cooled by running water. After 3 hours' standing the excess of permanganate was removed by the addition of alcohol and the colorless filtrate worked as usual for acids. Three and nine-tenths grams of pure benzoic acid, containing no trace of mandelic or benzoylformic acids, were obtained. As mentioned in the introduction, the results are quite different if the oxidation is carried on in the presence of caustic alkalies. Five grams of benzoyl carbinol, in 220 cc. of water, were added, in the cold, to a solution containing 11.60 grams of potassium permanganate (2 mols.) and 2.94 grams of sodium hydroxide (2 mols.), in 200 cc. of water. After 12 hours' standing the aqueous filtrate, when acidified with dilute sulphuric acid and extracted with ether, gave 5.3 grams of crude acid material. This was resolved into 2.3 grams of benzoylformic acid and 1.7 grams of benzoic acid.

Benzoylformaldehyde and Potassium Permanganate.—Two grams of benzoylformaldehyde, in 44 cc. of water, and a solution of 4.16 grams of potassium permanganate (2 mols.) in 75 cc. of water, gave, after standing 3 hours in the cold, 1.5 grams of pure benzoic acid. In an experiment using the same amounts of material as in the one just presented, but having, in addition, 1.04 grams of sodium hydroxide (2 mols.) present, 0.87 gram of benzoylformic acid and 1.2 grams of benzoic acid

were obtained. It is obvious that the benzoic acid formed in the experiment with permanganate alone may come, in the case of benzoyl carbinol, in part from an oxidation of the dissociated portions,

$$C_6H_5COCH_2OH \rightleftharpoons C_6H_5CHO + \diagdown\!\!\diagup CHOH.$$

In the presence of caustic alkali, however, as well as in all cases with benzoylformaldehyde, this must be formed *exclusively* from the oxidation of the dissociated benzoylformaldehyde hydrate molecules,

$$C_6H_5COCHO \rightleftharpoons C_6H_5\overset{H}{\underset{\diagup}{\diagdown}}CO + \diagdown\!\!\diagup CO.$$

Regarding the formation of benzoylformic acid in the experiments, it is certain that this results from an intermediate transformation of the benzoylformaldehyde by the caustic alkali present into *r*-mandelic acid, which, as will be shown directly, must oxidize at once under the conditions of the experiment to benzoylformic acid.

The formation of benzoylformic acid cannot possibly be ascribed to a *direct* oxidation of the molecular benzoylformaldehyde,

$$C_6H_5COCH(OH)_2 + O \rightarrow C_6H_5COCOOH + H_2O,$$

because, in that case, this acid should have been obtained from the aldehyde by aqueous permanganate alone and without the formation of any benzoic acid. Special experiments by Buchka and Irish[1] with potassium benzoylformate and an excess of permanganate prove that this acid is absolutely unchanged even after 14 days' standing, and this fact was confirmed. The benzoic acid, which is formed exclusively from benzoyl carbinol, as well as from benzoylformaldehyde with aqueous permanganate must, therefore, come from a burning of these molecules in the dissociated condition. When caustic alkali is present this is still one of the main results, but in that case

[1] Ber. d. chem. Ges., 20, 387. Cf. Beilstein: *Ibid.*, 17, 840.

there is about an equal amount of transformation of the benzoylformaldehyde into *r*-mandelic acid, which is then at once further oxidized.

The experiments of Nef[1] have shown very decisively that the free *r*-lactic acid is dissociated relatively *more* into acetaldehyde and formic acid,

$$CH_3CH(OH)COOH \rightleftarrows CH_3CHO + HCOOH,$$

whereas the salts of this acid, especially in the presence of caustic alkalies, which prevent hydrolysis and admit of further salt formation, are relatively *more* dissociated into water and ethylidenecarboxylic acid,

$$CH_3CH(OH)COOM \rightleftarrows CH_3(MOOC)C\diagup\diagdown + H_2O.$$

This explains why lactic acid in the free condition, or by the hydrolysis of its salts, *invariably* gives only acetic, formic and carbonic acids on treatment with oxidizing agents, and why the lactates, on the other hand, by the oxidation of the secondary alcohol group, invariably give acetylformic acid only. My own experiments with the analogous *r*-mandelic acid have confirmed in every way these conclusions of Nef and show that they apply, word for word, in this case also. Beilstein has shown[2] that *r*-lactic acid with alkaline permanganate solutions in the cold, gives a large yield of pyruvic acid. I have found that *r*-mandelic acid, under similar conditions, even when a great excess of alkaline potassium permanganate is added, gives benzoylformic acid quantitatively. This is, in fact, by far the best method for preparing benzoylformic acid. It is important to realize that an excess of alkali should be present, in which case no trace of benzoic acid can be formed. If free mandelic acid, or even a mandelate, be treated, in aqueous solution, with potassium permanganate, there is a chance for formation of some benzoic acid, because free mandelic acid, formed by hydrolysis, must be present and this gives, by oxidation, benzoic and carbonic acids only, because it is dissociated mainly according to the scheme

[1] Ann. Chem. (Liebig), 335, 296.
[2] *Loc. cit.*

$$C_6H_5CH(OH)COOH \rightleftharpoons C_6H_5CHO + HCOOH.$$

Benzoyl Carbinol and Silver Oxide.—Three grams of benzoyl carbinol, dissolved in 300 cc. of water, were added to 2.25 mols. of freshly precipitated and well washed silver oxide, from 16.8 grams of silver nitrate; no action takes place until the temperature is raised to 70°. After heating 4 hours on a boiling water-bath, during which time a steady stream of carbon dioxide was evolved, the reduction to silver was complete. One and nine-tenths grams of benzoic acid, 0.30 gram of unchanged carbinol and 10 grams of silver were the only reaction products. In a second experiment, using 4 grams of carbinol, silver oxide from 20 grams of silver nitrate (4 mols.), 4.7 grams of sodium hydroxide (4 mols) and water (total volume 350 cc.), reduction took place rapidly at the ordinary temperature. Pure benzoic acid, 3.32 grams = 92 per cent of the theoretical amount, and 12.60 grams of silver were the only products found.

Benzoylformaldehyde and Silver Oxide.—One gram of benzoylformaldehyde hydrate, dissolved in 75 cc. of water, was treated with 1.25 mols. of freshly precipitated and well washed silver oxide, from 2.52 grams of silver nitrate. No action took place on standing over night. Therefore the mixture was heated for 3 hours, at 70°–100°, when a copious evolution of carbon dioxide was observed. There were obtained 0.75 gram of pure benzoic acid, 92 per cent of the theory, silver and carbon dioxide, as the only reaction products. On repeating the experiment, having, in addition, 1.32 grams of sodium hydroxide (2 mols.) present, a reduction of silver took place at once, in the cold. Eight-tenths of a gram of pure benzoic acid, 1.77 grams of silver and only a few milligrams of *r*-mandelic acid were obtained.

Mandelic Acid and Silver Oxide.—In a special experiment with 1 gram of mandelic acid, 1 mol. of freshly precipitated silver oxide, 0.53 gram = 2 mols. of sodium hydroxide and 50 cc. of water, it was found that no trace of reduction to silver took place on heating for 6 hours on a boiling water-bath; the acid was, furthermore, recovered entirely unchanged. Two and

eight tenths grams of pure silver mandelate,[1] dissolved in 350 cc. of water and treated on a boiling water-bath for 4 hours, with 2 mols. of freshly precipitated and well washed silver oxide, from 8.10 grams of silver nitrate, gave, on working up in the usual manner, 0.40 gram of benzoic acid, besides 0.55 gram of unchanged *r*-mandelic acid, but no trace of benzoylformic acid. These results are in harmony with the work of Nef[2] on lactic acid. The observations prove, therefore, with great precision, that no mandelic acid can have been formed as an intermediate product in the action of silver oxide alone, or in the presence of sodium hydroxide, on benzoyl carbinol or benzoylformaldehyde, respectively.

Benzoylformic Acid and Silver Oxide.—Silver oxide, in the presence of sodium hydroxide, is without effect on benzoylformic acid in the cold. On heating to 100°, however, reduction to silver and a quantitative transformation to carbonic and benzoic acids takes place. Thus a mixture of 0.50 gram of benzoylformic acid, 0.52 gram of sodium hydroxide, 1 mol. of silver oxide and 25 cc. of water gave, on heating during 3 hours, at 100°, 0.40 gram of benzoic acid.

One and two-tenths grams of silver benzoylformate, dissolved in 300 cc. of water containing 1.25 mols. of well washed silver oxide, remained unchanged after 3 hours' heating at 30°, but, on heating at 100°, carbon dioxide began to be evolved and, after 3 hours' heating, 0.50 gram of pure benzoic acid was obtained as a reaction product.

These experiments prove that benzoylformic acid cannot have been formed as an intermediate product in the action of silver oxide alone, or in the presence of caustic alkalies, on benzoyl carbinol or benzoylformaldehyde ; it is certain, therefore, that the benzoic and carbonic acids obtained in these cases result from a direct oxidation of the dissociation products of benzoylformaldehyde,

$$C_6H_5COCHO \rightleftharpoons C_6H_5CHO + \diagdown\!\!\diagup CO,$$

[1] Winckler : Ann. Chem. (Liebig), **18**, 310.
[2] *Ibid.*, **335**, 277, 297, 315.

which, in these instances, cannot recombine to form *r*-mandelic acid because their speed of oxidation must be far more rapid than the velocity of the benzilic acid rearrangement.

The corresponding experiments, using freshly precipitated mercuric oxide in place of silver oxide, lead to exactly the same conclusions; they are, therefore, simply mentioned here without further comment.

Benzoyl Carbinol and Mercuric Oxide.—Five grams of benzoyl carbinol, dissolved in 350 cc. of water, were treated with an emulsion of freshly precipitated mercuric oxide, from 22 grams of mercuric chloride, in 200 cc. of water. No action took place in the cold, but on heating for 9 hours on a water-bath, much carbon dioxide was evolved. Pure benzoic acid, 3.75 grams = 83 per cent of the theoretical, besides 0.35 gram of unchanged carbinol were obtained as reaction products. In a second experiment, using the same amounts of material, but adding also a solution of 6 grams of sodium hydroxide in 50 cc. of water, reduction to mercury took place at once, in the cold; after 12 hours' standing, 4.10 grams of pure benzoic acid = 91.3 per cent of the theory, were obtained.

Benzoylformaldehyde and Mercuric Oxide.—One gram of benzoylformaldehyde hydrate, dissolved in 75 cc. of water, was treated with 1.25 mols. of freshly precipitated mercuric oxide and thereupon a solution of 0.52 gram of sodium hydroxide (2 mols.) in 25 cc. of water were added. Reduction took place at once, in the cold and, after 12 hours' standing, 0.85 gram (theory 0.88 gram) of pure benzoic acid was obtained, but no trace of mandelic acid.

A special experiment with 2 grams of mandelic acid, 1 mol. of precipitated mercuric oxide and 1.60 grams of sodium hydroxide, in 50 cc. of water, proved that no reduction to mercury took place, even on heating 2.5 hours on a water-bath; 1.90 grams of mandelic acid were subsequently recovered unchanged. Finally, it should be emphasized, that my results with mercuric oxide and benzoyl carbinol are in accord with the corresponding ones obtained by Nef with acetol.[1] Kling[2]

[1] Ann. Chem. (Liebig), **335**, 276.
[2] Bull. Soc. Chim., [3], **33**, 1, **34**, 49.

states that acetol is converted by mercuric hydroxide *quantitatively* into lactic acid ; this is obviously a mistake.

On the Behavior of Benzoyl Carbinol, Benzoylformaldehyde, Mandelic Acid and Benzoylformic Acid towards Chromic and Dilute Sulphuric Acids.—The following quantitative experiments, which show that these substances give benzoic and carbonic acids only, on oxidation in the cold with chromic acid in dilute sulphuric acid solution, are simply recorded here ; they require no further elucidation :

a. A mixture of 5 grams of benzoyl carbinol, 8.10 grams of potassium dichromate (2.25 atoms of oxygen), 10.8 grams of sulphuric acid and 400 grams of water gave, after standing 2 days in the cold, 2.10 grams of benzoic acid and 1.70 grams of unchanged carbinol.

b. One-half gram of benzoylformaldehyde hydrate, 0.74 gram of potassium dichromate, 0.97 gram of sulphuric acid and 70 cc. of water gave, after 2 days' standing in the cold, 0.44 gram of pure benzoic acid.

c. One gram of mandelic acid, 1.46 grams of potassium dichromate, 5.76 grams of sulphuric acid and 70 cc. of water gave, on standing 24 hours in the cold, 0.75 gram of benzoic acid.

d. One-half gram of benzoylformic acid, 0.41 gram of potassium dichromate, 0.60 gram of sulphuric acid and 50 cc. of water gave, on standing over night in the cold, 0.40 gram of benzoic acid.

PART II.

ON THE BEHAVIOR OF BENZOYL CARBINOL TOWARDS ALKALIES ; A REVISION OF PAAL AND SCHULZE'S WORK ON THE α- AND β-HALOGEN DIPHENACYLS.

On treatment of acetol, with caustic alkalies, under the most varied conditions, Nef never obtained a trace of *r*-lactic acid but mainly neutral, deep red colored resins which were considered by him to be polymerized acetylmethylene resin.[1] Benzoyl carbinol behaves in an entirely similar manner towards caustic alkalies, as well as towards alcoholic potassium hy-

[1] Ann. Chem. (Liebig), 335, 278.

droxide and sodium ethylate. A small quantity of benzoic acid, entirely free from traces of *r*-mandelic acid, is invariably formed; the main reaction products, however, consist of dark yellow, non-volatile resins, in which no trace of *cis*- or *trans*-dibenzoylethylene,[1] but at times traces of *trans*-tribenzoylcyclotrimethylene, melting at 295°,[2] were found. The resins obtained could, moreover, never be converted into solids or into crystalline derivatives.

Since the monohalogenated acetophenones give, on treatment with various reagents, such as sodium acetoacetic ether, ammonia and, especially, with alcoholic potassium hydroxide or sodium ethylate (one-half mol.) large quantities of so-called space isomeric α- and β-halogen diphenacyls,[3] it was thought possible that oxyacetophenone might, on similar treatment, first give the corresponding space isomeric α- and β-oxydiphenacyls; consequently, attempts were made to obtain these products first by synthesis directly from the so-called α- and β-bromdiphenacyls. Paal and Schulze have made an especially exhaustive study of these two compounds.[4] They find that they are totally different from the *real* γ-bromdiphenacyl,

$$C_6H_5COCHBrCH_2COC_6H_5,$$

obtained from *cis*- and *trans*-dibenzoylethylene and hydrogen bromide. In view of the fact that their products give, by reduction, small amounts of diphenacyl or its corresponding glycol,

$$C_6H_5CH(OH)CH_2CH_2CH(OH)C_6H_5,$$

and because a fourth isomeric, so-called δ-halogen diphenacyl was isolated, Paal and Schulze give to their α- and β-compound the following dienol formula,

$$C_6H_5C(OH) : CBrCH : C(OH)C_6H_5,$$

which is, obviously, capable of giving four different space isomers.

[1] Ber. d. chem. Ges., **33**, 3784; **35**, 168.

[2] Paal and Schulze: *Ibid.*, **36**, 2425.

[3] Fritz: *Ibid.*, **22**, 3028. Paal and his students: *Ibid.*, **19**, 3146; **22**, 3225; **28**, 2102; **29**, 2092; **32**, 530; **36**, 2405.

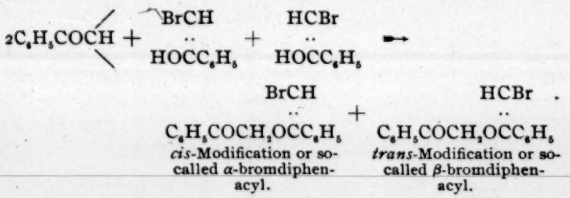
[4] Ber. d. chem. Ges., **36**, 2386, 2405, 2415, 2425.

Further consideration shows, however, a great many serious objections to the formulae proposed by Paal and Schulze for their α-, β- and δ-compounds. It is noteworthy, (1) that they were never able to prove the presence of hydroxyl groups in their substances; (2) the compounds do not go over into furfuran derivatives by loss of water; (3) the α- and β-compounds have never been converted into the real γ-bromdiphenacyl, or *vice versa*, nor into one of the space isomeric dibenzoylethylenes.

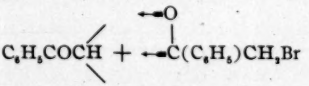
On the other hand, the real γ-halogen diphenacyls go over quantitatively, even on standing, and especially on heating with sodium acetate and acetic acid, into *trans*-dibenzoylethylene.

In the present state of our knowledge there are, moreover, two other possible interpretations[1] of the reaction between bromacetophenone and sodium ethylate.

I. The benzoylmethylene, resulting from the dissociation of bromacetophenone, may react by alkylation with unchanged bromacetophenone *in the enol form*, and thus give rise to two space isomeric *cis*- and *trans*-α-phenacyloxy-ω-bromstyrols:



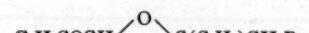
II. The benzoylmethylene might react with the active ketobromacetophenone molecules present,



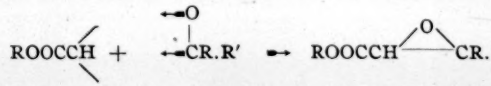
giving, by addition,[2] a glycid derivative,

[1] Cf. Nef: Ann. Chem. (Liebig), **310**, 316; **335**, 252, 261.

[2] Cf. Nef: *Ibid.*, **335**, 274. Foot-note.



which can exist in two space isomeric modifications. Professor Nef informs me that he believes the recent work of Claisen[1] and Darzens[2] on the conversion of ketones and some aldehydes into glycid derivatives by means of chloracetic ether, in the presence of sodium ethylate or sodamide, can only be rationally interpreted on this basis,[3] *i. e.*, the methylenecarboxylate, present as a product of dissociation of chloracetic ether, simply unites with the various active ketone or aldehyde molecules present thus:



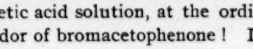
Interpretation II. cannot, however, possibly apply to the α- and β-halogendiphenacyl derivatives under consideration, because there is absolutely nothing known in their behavior justifying the presence of a glycid group. Consequently, we are forced to turn back to interpretation I. On looking over the work of Paal and Schulze on α- and β-bromdiphenacyl, it is noteworthy that one finds there a great deal of evidence in favor of the new formulae given under I. for these compounds—as, for instance, the absence of hydroxyl groups, the impossibility of converting these compounds into the real γ-bromdiphenacyl and *vice versa*, or into dibenzoylethylene or furfuran derivatives.

The most striking observation, repeatedly made, is the fact that α- and β-bromdiphenacyl, on treatment with dry halogen hydrides, in acetic acid solution, at the ordinary temperature, give a strong odor of bromacetophenone! If the so-called α- and β-bromdiphenacyls have the constitution assigned to them

[1] Ber. d. chem. Ges., 38, 693.

[2] Centrabl., 1905, I, p. 346.

[3] A similar interpretation obviously applies to the formation of the product



obtained recently by Torrey from *p*-nitrosodimethylaniline and ethyl bromide. THIS JOURNAL, 34, 475 (1905).

above under I. they, or their addition products, must be resolved, quantitatively, in the cold, by dry hydrogen bromide, either into equal molecules of bromacetophenone and ω-dibromphenylmethylcarbinol, $C_6H_5CH(OH)CHBr_2$, or into 2 mols. of bromacetophenone. I propose, therefore, to carry out experiments in this direction at once. I have found, moreover, that α- and β-bromdiphenacyls give, on treatment with fused sodium acetate in acetic acid solution, at 100°, 66–68 per cent of the theoretical amounts, *viz.*, 2 mols. of benzoyl carbinol acetate (see below). The isomeric α- and β-acetoxydiphenacyls, as well as the β-oxydiphenacyl, also give a large yield of benzoyl carbinol acetate on similar treatment. These results are self-evident on the basis of the new formulæ for the compounds, but cannot be understood on the basis of those of Paal and Schulze. It should be remembered that the real, so-called γ-bromdiphenacyl gives, quantitatively, on treatment with sodium acetate and acetic acid, *trans*-dibenzoylethylene. The only observation which points in any way towards the old formulae is the conversion of α- and β-bromdiphenacyl, by reduction with zinc dust and alcohol, into diphenacyl. This experiment was, therefore, repeated with the following result: Only a very small amount, about 10 per cent, of diphenacyl and about an equal quantity of acetophenone are formed. The main reaction product is a non-volatile oil—probably α-phenacyloxystyrol, $CH_2 : C(C_6H_5)OCH_2COC_6H_5$, which at present is being further investigated. The formation of small quantities of diphenacyl in the above experiment is not difficult to understand on the basis of the new formulae; one has only to remember that Claisen's analogous O-ethylacetophenone,[1]

$$CH_2 : C(C_6H_5)OC_2H_5,$$

undergoes rearrangement by heat (for the explanation, *vide* Nef[2]) into C-ethylacetophenone, $C_6H_5COCH_2C_2H_5$. Furthermore, I have found that a mixture containing acetophenone and bromacetophenone, when heated in a sealed tube at 100°, with 10 per cent aqueous sodium hydroxide gives, among other

[1] Ber. d. chem. Ges., **29**, 2931.
[2] Ann. Chem. (Liebig), **298**, 372; **310**, 316.

products, a very fair yield of diphenacyl—*i. e.*, an alkylation of acetophenone by benzoylmethylene[1] takes place. It is, therefore, exceedingly probable that the small amount of diphenacyl obtained by Paal and Fritz in their experiments was formed in some such manner.

Finally, I consider the existence of the fourth so-called δ-ioddiphenacyl of Paal and Schulze as extremely doubtful; I think that it consists simply of the pure β-isomer; as has been shown by Paal and Schulze, it certainly gives exactly the same reactions and derivatives as the so-called β-compound and possesses, practically, the same crystalline form.[2]

Although, in view of what has just been presented, I consider the formulae of Paal and Schulze as practically untenable, I still use, in the following experimental part, their nomenclature for the α- and β-substituted diphenacyl derivatives. It is my intention to continue the study of these derivatives and to include also a study of the corresponding compounds in the aliphatic series.

The Conversion of α- and β-Bromdiphenacyl into Two Molecules of Benzoyl Carbinol Acetate.—On treating bromacetophenone with 0.5 mol. of alcoholic sodium ethylate and allowing the mixture to stand at 0° for 2 days, I obtained about equal quantities of α- and β-bromdiphenacyl;[3] these were separated according to the directions of Paal, by means of cold benzene.

A solution of 1.55 grams (2 mols.) of fused sodium acetate, in 12 grams of glacial acetic acid, was cooled to 30°, 3 grams of β-bromdiphenacyl were added and the mixture heated for 6 hours, under a reversed condenser, in an oil-bath which was kept at 120°–130°. On pouring the dark red mixture into water, extracting with ether and washing with sodium carbonate solution, 3.10 grams of a dark brown oil were obtained. On distillation this gave 2.30 grams of pure benzoyl carbinol acetate, melting at 49°–50° and boiling at 160°–163° (18–20 mm.); this corresponds to 68 per cent of the theoretical amount. The

[1] Cf. Nef: Ann. Chem. (Liebig), **310**, 316.
[2] Ber. d. chem. Ges., **36**, 2411–2413.
[3] Cf. Fritz: *Ibid.*, **28**, 3028. Also Paal and Demeler: *Ibid.*, **29**, 2092.

product was further identified by its conversion by boiling water (*vide* Part I.) into benzoyl carbinol, melting at 86°.

A similar experiment with 3 grams of α-bromdiphenacyl, under practically the same conditions as in that just described, gave 0.50 gram of a reddish, non-volatile tar and 2.20 grams of pure benzoyl carbinol acetate, or 65.3 per cent of the theory.

The Conversion of α- and β-Acetoxydiphenacyl into Benzoyl Carbinol Acetate.—Paal and Schulze obtained β-acetoxydiphenacyl, melting at 98°, from the β-brom- or iodo-, as well as from the δ-ioddiphenacyl, on boiling with silver acetate and glacial acetic acid;[1] this compound can be best obtained, as I have found, by heating a mixture of 4 grams of β-bromdiphenacyl, 3.82 grams of potassium acetate and 40 cc. of absolute alcohol, for 3 hours, in a sealed tube, at 100°. An odor of acetic ether was noticed on opening the tube, and, on adding water, extracting with ether and crystallizing from ether-ligroin, 2.65 grams of pure product, 71 per cent of the theory, were obtained. Two grams of this were heated in a bath, at 120°–130°, for 5 hours, with a solution of 1.04 grams of fused sodium acetate and 5 grams of glacial acetic acid. On working up as in the previous cases, 0.88 gram of non-volatile tar and 0.90 gram of pure benzoyl carbinol acetate, boiling at 153° (12 mm.) and melting at 49°–50°, were obtained; this is 37 per cent of the theoretical amount.

According to Paal and Schulze, the α-bromdiphenacyl does not give the corresponding α-acetoxydiphenacyl on boiling with silver acetate and acetic acid; two isomeric, high-melting compounds, $(C_8H_4O_4)_4$, which they call bisanhydrooxydiphenacyl, or tetrabenzoyltetramethylene, were obtained.[2] Such a compound, $(C_8H_4O_4)_4$, could, naturally, also be formed from the *cis*-ω-brom-α-phenacyloxystyrol,

$$C_6H_5COCH_2OCC_6H_5$$
$$\quad\quad\quad

above. I have, however, succeeded in obtaining totally different results by the action of alcoholic potassium acetate, 3.38 grams, on 3.75 grams of α-bromdiphenacyl, in a sealed tube, at 100°. Three and three-tenths grams of a thick, yellow oil were obtained, which I believe to be the crude α-acetoxydiphenacyl; it could not be obtained in a solid condition, but 2 grams of it, heated with sodium acetate and acetic acid, under exactly the same conditions as the β-acetate just described, gave 0.75 gram of non-distillable tar and 0.95 gram of pure distilled benzoyl carbinol acetate; this corresponds to 39.6 per cent of the theory.

β-Oxydiphenacyl.—On saponification of the β-acetoxydiphenacyl with alcoholic potassium hydroxide, Paal and Schulze obtained a yellow oil which, by treatment with sodium acetate and acetic anhydride, was converted back again into the original acetate; it must, therefore, have contained oxydiphenacyl. I have succeeded in obtaining β-oxydiphenacyl in the crystalline form; it is formed, besides an oily substance, not only from β-bromdiphenacyl, but also, probably by rearrangement into the β-space isomer, in smaller amounts (22 per cent yield) from α-bromdiphenacyl, by heating 2 grams of these compounds in 20 cc. of a methyl alcoholic solution of 1.5 mols. of potassium formate,[1] in sealed tubes, for 6 hours, at 100°. In the case of the β-isomer 0.95 gram of pure β-oxydiphenacyl was obtained, or 59 per cent of the theory; as the substance is very difficultly soluble in cold benzene and ether, it could readily be freed from a small amount, 0.65 gram, of the oily product. Crystallization from hot benzene gave microscopic needles of β-oxydiphenacyl, melting at 175°–178°. In the α-series 0.35 gram of the β-oxy compound and 1.25 grams of yellow oil were obtained. Analysis of the crystalline product:

0.1874 gram substance gave 0.5204 gram CO_2 and 0.0984 gram H_2O.

	Calculated for $C_{16}H_{14}O_2$.	Found.
C	75.59	75.72
H	5.51	5.83

[1] Nef: Ann. Chem. (Liebig), **335**, 260, 265.

A mixture of 1 gram of β-oxydiphenacyl, 0.64 gram of fused sodium acetate and 7.10 grams of glacial acetic acid, heated in an oil-bath, at 130°, for 6 hours, gave 0.40 gram of pure distilled benzoylcarbinol acetate and 0.30 gram of non-volatile tar. It should be emphasized, in this connection, that benzoyl carbinol itself, on heating under the same conditions with sodium acetate and acetic acid, remains entirely unchanged.

One and one-half grams of β-oxydiphenacyl, heated for 6 hours, at 130°, with 6 grams of acetic anhydride, gave 0.6 gram of β-acetoxydiphenacyl, melting at 98°–98°.5.

The question now arises whether any β-oxydiphenacyl is formed by the action of caustic alkalies on oxyacetophenone according to the equation,

$$HOCH : C(C_6H_5)OH + \begin{matrix} \diagdown \\ \diagup \end{matrix} CHCOC_6H_5 + H_2O \rightarrow$$

Enol modification of benzoyl carbinol. — Dissociated benzoyl carbinol.

$$HOCH : C(C_6H_5)OCH_2COC_6H_5.$$

I can simply state here that none was found; it is, however, exceedingly probable that a compound of this constitution must, under the conditions employed, take up water to form the isomeric aldehyde,

$$HCOCH(C_6H_5)OCH_2COC_6H_5,$$

and this, by loss of water, can easily go over into a condensation product. Interpreted on this basis, the condensation product, $C_6H_8O_2$, obtained by Peratoner and Leonardi,[1] from acetol and aqueous barium hydroxide, must possess the constitution,

$$\begin{matrix} CH_3CHOCH_2 \\ | \\ CH : CH \end{matrix} \diagdown\diagup CO;$$

i. e., it must be 1-methyl-4-keto-Δ^2-dehydrohexone, being formed from β-acetonyl-α,β-dihydroxypropylene,

$$HOCH : C(CH_3)OCH_2COCH_3,$$

[1] Gazz. chim. ital., 30, 1, 577.

or the corresponding aldehyde, by loss of water. This corresponds, in general, very closely to the formula,

2-methyl-4-keto-Δ^2-dehydrohexone, assigned to it by Peratoner and Leonardi, and explains all the known reactions of the compound equally well. In view of this, I am encouraged to study still further the yellow tars obtained by the action of caustic alkalies on acetol and benzoyl carbinol, respectively.

On the Reduction of β-Bromdiphenacyl by Zinc Dust and Alcohol.—On treatment of β-bromdiphenacyl with these reagents, V. Fritz[1] obtained small quantities of diphenacyl and acetophenone; this observation was confirmed by Paal and Demeler,[2] who state that, in addition, a large amount of non-volatile oil is formed. I have repeated this experiment with 8 grams of material, 40 grams of zinc dust and 100 cc. of ethyl alcohol, heating 2.5 hours on a boiling water-bath. Five and one-tenth grams of crude reaction product were obtained on filtering, adding water and extracting with ether. The acetophenone was removed by heating in a bath up to 160° (18 mm.); only 0.5 gram was thus obtained and identified by conversion into the phenylhydrazone.[3] Three-tenths gram of diphenacyl, melting at 140°–142°, and converted into the characteristic dioxime,[4] melting at 202, were obtained from the oil left on adding a small amount of alcohol and stirring. The remainder, 4.30 grams, and, therefore, the main reaction product, consisted of a thick, non-volatile oil, whose study is to be continued. It is, in all probability, α-phenacyloxystyrol,

$$CH_2 : C(C_6H_5)OCH_2COC_6H_5,$$

isomeric with diphenacyl and, therefore, formed by a direct reduction of β-bromdiphenacyl.

[1] Ber. d. chem. Ges., **28**, 3033.
[2] *Ibid.*, **29**, 2096.
[3] Bischler: *Ibid.*, **16**, 662.
[4] Paal and Kapf: *Ibid.*, **31**, 3057.

In conclusion, I wish to acknowledge my deep sense of gratitude to Professor Nef for his inspiring and careful guidance of this work.

THE GERMICIDAL ACTION OF POTASSIUM PERMANGANATE.

By James B. Garner and Walter E. King.

INTRODUCTORY PAPER.

The use of solutions of potassium permanganate as a disinfecting agent has been extensive and popular, from the standpoint of both efficiency and economy. Accurate details regarding the antiseptic and germicidal action of potassium permanganate upon *B. typhosus* seem to be lacking. Jäger's and Miquel's[1] statements are only approximate ones. Jäger says that a 5 per cent solution (approximately N/1.6) of potassium permanganate is a germicide to all pathogenic organisms, excepting tubercle bacillus, and that a 1 per cent solution (approximately N/0.32) is not reliable for the destruction of these same organisms. According to Miquel, potassium permanganate is an antiseptic in the proportion of 1 : 285 (approximately N/0.091).

Our preliminary experiments, made upon a pure 24-hour bouillon culture of *bacillus typhosus*, with dilute solutions of potassium permanganate, lead us to believe that the reagent is antiseptic and germicidal in less quantities than those given by Miquel and Jäger. The results of these preliminary experiments, therefore, occasioned the work of this introductory paper on the general subject of the germicidal action of potassium permanganate. We purpose to study closely the action of solutions of this reagent upon all of the common pathogenic organisms.

Methods.

In conducting the experiments all apparatus, including pipettes, burettes, test tubes, flasks, graduates, etc., was sterilized and all possible precautions were observed to avoid

[1] "Sternberg's Bacteriology," p. 186.

contamination. One-half liter quantities of sterile, distilled water, in sterile glass flasks, were used in the 8 series. Each series consisted of 2 flasks of sterile water, to each of which 1 cc. of a pure, 24-hour bouillon culture of *B. typhosus* was added, thus affording a means of checking results. Varying volumes of N/6000, N/4000, N/1000 and N/10 solutions of potassium permanganate were added to the several flasks containing the water and culture. The mixtures were incubated and, after varying periods of incubation, the ordinary methods were followed to determine the presence or absence of organisms.

EXPERIMENTAL PART.

In each of the 2 flasks of the 8 series given below, 500 cc. of sterile, distilled water were used, varying amounts of potassium permanganate solutions were added, as indicated for the different series, then 1 cc. of a pure 24-hour bouillon culture of *B. typhosus*, excepting in Series V. The temperature of the incubation was 37°.4 and the periods of growth were from 24–72 hours:

Series I.—Flasks (*a*) and (*b*), 25 cc. N/6000 potassium permanganate were added. Total volume, 526 cc.

Series II.—Flasks (*a*) and (*b*), 20 cc. N/4000 potassium permanganate were added. Total volume, 521 cc.

Series III.—Flasks (*a*) and (*b*), 20 cc. N/1000 potassium permanganate were added. Total volume, 521 cc.

Series IV.—Flasks (*a*) and (*b*), 10 cc. N/10 potassium permanganate were added. Total volume, 511 cc.

Series V.—Flasks (*a*) and (*b*), no potassium permanganate added. *Check flasks.* Total volume, 501 cc.

Series VI.—Flasks (*a*) and (*b*), 25 cc. N/6000 and 12.6 cc. N/10 potassium permanganate solutions were added. Total volume, 538.6 cc.

Series VII.—Flasks (*a*) and (*b*), 20 cc. N/4000 and 20.1 cc. N/10 potassium permanganate solutions were added. Total volume, 541.1 cc.

Series VIII.—Flasks (*a*) and (*b*), 20 cc. N/1000 and 50.3 cc.

Tabulation of Results.

Series.	Volume of permanganate.	Total volume.	Concentration of permanganate.	Growth checked.
I., *a* and *b*	25 cc. N/6000	526 cc.	N/126260	——
II., *a* and *b*	20 cc. N/4000	521 cc.	N/104200	——
III., *a* and *b*	20 cc. N/1000	521 cc.	N/26050	——
IV., *a* and *b*	10 cc. N/10	511 cc.	N/511	Growth inhibited, 67 colonies per cc.
V., *a* and *b*	None	501 cc.		Check flasks, 4050 colonies per cc.
VI., *a* and *b*	25 cc. N/6000 12.6 cc. N/10	538.6 cc.	N/426.6	+
VII., *a* and *b*	20 cc. N/4000 20.1 cc. N/10	541.1 cc.	N/213.35	+
VIII., *a* and *b*	20 cc. N/1000 50.3 cc. N/10	571.3 cc.	N/113.06	+

N/10 potassium permanganate solutions were added. Total volume, 571.3 cc.

After all the flasks had remained in the incubator for 24 hours, tubes of sterile bouillon, 15 cc. each, were inoculated with 1 cc. from each flask. These bouillon tubes were incubated for 24 hours; cloudy growth was noted in all tubes of Series I., II., III. and V.; slower growth was shown, however, in the tubes inoculated with samples from Series IV., (*a*) and (*b*), and not until the end of 33 hours' incubation did these tubes show a uniform cloudy growth. Tubes from Series VI., VII. and VIII. remained clear after 48 and 72 hours' incubation. Three repetitions of these inoculations gave the same results.

Agar plates were inoculated with 1 cc. from flask (*a*), Series IV. After 48 hours' incubation the average colony count showed 67 per cc.

An agar plate was inoculated with 1 cc. from flask (*a*), Series V. After 32 hours' incubation 4050 colonies per cc. were estimated.

In the above experiments all cultures were studied in regard to morphology and cultural characters and no contaminations were observed.

The results obtained from the flasks of Series IV. indicate that N/511 potassium permanganate is antiseptic to *B. typhosus*.

The mixtures in the flasks resulting from experiments, Series VI. to VIII., inclusive, were of a rose color, thus indicating an excess of permanganate. An excess of 0.00245 gram permanganate was found in flasks (*a*) and (*b*) of Series VI., by titration with standard ferrous ammonium sulphate solution, in presence of dilute sulphuric acid. This excess, deducted from the total quantity added, left the amount of permanganate which was germicidal to *B. typhosus*. The concentration calculated is N/458.

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Contributions from the Chemical Laboratory of Harvard College.

ON ORTHOPARADIBROMORTHOPHENYLENEDIAMINE.

By C. Loring Jackson and F. W. Russe.

The substance described in this paper was prepared in the hope that a diamine containing bromine might convert tetrabromorthoquinone into a quinoxaline, but it acted no better than the orthophenylenediamine itself, giving, like that, red amorphous products, which we think were formed by oxidation of the amino groups.

We tried first to make the tetrabrom derivative by the action of bromine on orthophenylenediamine, but could obtain only red amorphous substances, which we think are identical with those mentioned in the preceding paragraph. We next prepared the 2,4-dibromorthonitraniline of Remmers,[1] reduced it to the new orthoparadibromorthophenylenediamine and tried the action of bromine on this, but with similar bad results. Accordingly, we gave up the attempt to make the tetrabrom compound and studied the orthoparadibromorthophenylenediamine, $C_6H_2Br_2(NH_2)_2$, obtained as described above. This melts at 83° and, therefore, has the constitution $NH_2 = 1,2$; $Br_2 = 4,6$, as the 4,5-dibromorthophenylenediamine, melting at 137°, has been made by Schiff,[2] and the only other possible isomer, 3,6-dibromorthophenylenediamine, melts at 94°–95°, and was made by Calhane and Wheeler.[3]

With hydrochloric acid the orthoparadibromorthophenylenediamine gave a monohydrochloride, $C_6H_2Br_2(NH_2)NH_2Cl$, stable in the air but decomposed by hot water, whereas with hydrobromic acid, under the same conditions, a dihydrobromide, $C_6H_2Br_2(NH_2Br)_2$, seemed to be formed, which was so unstable that we did not succeed in obtaining it in a state of purity. Acetic anhydride converted our diamine into the diacetamide, $C_6H_2Br_2(NHC_2H_3O)_2$, which melts at 227°–228°. With phenanthrenequinone it formed the quinoxaline,

[1] Ber. d. chem. Ges., 7, 349 (1874).
[2] Sitzun. Wien., 99, 2b, 361 (1890).
[3] This Journal, 22, 452 (1899).

$$C_6H_2Br_2N_2C_2(C_6H_4)_2,$$

which melts at 248°, whereas Schiff's 4,5-compound melts at 286° and Calhane and Wheeler's 3,6-body at 297°. With benzil our dibromorthophenylenediamine gave

$$C_6H_2Br_2N_2C_2(C_6H_5)_2,$$

melting at 149°-150°, the 3,6-compound melts at 215°–216°.

Hinsberg[1] found that diphenylenequinoxaline itself gave a deep red color with all the strong mineral acids; our two quinoxalines gave such a color with strong sulphuric acid, but were not turned red by strong hydrochloric acid or nitric acid, although the phenanthrene compound was reddened by fuming nitric acid. The dibromquinoxalines of Calhane and Wheeler[2] behaved like ours in regard to acids.

The replacement of bromine by hydrogen during the reduction of aromatic compounds with tin and hydrochloric acid has been observed[3] in many cases, but in all of these the groups containing nitrogen were in the meta position to each other with two exceptions, one of which was the reduction of symmetrical tribromaniline to dibromaniline[4] and the other the formation of a small quantity of orthophenylenediamine from parabromorthonitraniline, observed by Hübner.[5] As the yield of our dibromorthophenylenediamine was very small, we thought it possible that such a reaction might have taken place, but a careful search failed to show orthophenyldiamine in our reduction product. We confirm, therefore, the results previously obtained and it is evident that orthonitro compounds have little tendency to lose bromine under the action of tin and hydrochloric acid.

EXPERIMENTAL.

The 2,4-dibrom-6-nitraniline was prepared by adding bromine, diluted with a little acetic acid, to a solution of orthonitraniline in 10 times its weight of acetic acid, in the proportion of

[1] Ann. Chem. (Liebig), **237**, 340 (1887).
[2] THIS JOURNAL, **22**, 457 (1899).
[3] Jackson and Calvert: *Ibid.*, **18**, 465 (1896).
[4] *Ibid.*, **18**, 480 (1896).
[5] Ann. Chem. (Liebig), **209**, 360 (1881).

2 molecules of bromine to 1 of the base. The bromine disappeared instantly, with a slight evolution of heat. The product was precipitated by the addition of water and, after a thorough washing, recrystallized once from dilute alcohol, which raised the melting point to 127°, that observed by Remmers.[1] The yield was quantitative.

An excess of bromine gave no further action, even when the mixture was boiled for 5 hours in a flask with a return condenser.

Preparation of Orthoparadibromorthophenylenediamine, $C_6H_2Br_2(NH_2)_2$.—The reduction of the 2,4-dibrom-6-nitraniline was effected most conveniently with tin and hydrochloric acid, as this gives a white product, whereas zinc and acetic acid frequently give a brownish diamine, which, however, is essentially pure, as it melts at the same point as the white one.

The dibromnitraniline, moistened with a little alcohol, was warmed with 50 times its weight of hydrochloric acid and an excess of tin in a flask, on the steam-bath, until the yellow color of the nitraniline had disappeared. An excess of potassic hydrate was then added and the solution distilled, when the dibromorthophenylenediamine passed over. As the water distilled off more was added, taking care not to dilute the solution too much, since the diamine does not begin to volatilize until the boiling point of the solution reaches 123°. The product obtained in this way was pure. The diamine was also prepared by reduction with zinc and acetic acid, which had the advantage that it was not necessary to isolate the solid dibromnitraniline, but finely granulated zinc could be added directly to the acetic acid solution in which the dibrom product was formed. If the solid nitraniline was used, 5 grams of it were mixed with 50 grams of glacial acetic acid and an excess of finely granulated zinc, water was then added until there was an active evolution of hydrogen and the mixture allowed to stand over night at 60°–70°. The product, disregarding any crystals of zincic acetate which had separated, was treated with an excess of sodic hydrate and distilled, as already described. The yield by either

[1] Ber. d. chem. Ges., 7, 349 (1874).

process was about 5 per cent of the weight of the dibromnitraniline. Some of the diamine filtered from the distilled water was dried in a desiccator for analysis:

0.1547 gram substance gave 0.2177 gram AgBr.

	Calculated for $C_6H_2Br_2(NH_2)_2$.	Found.
Br	60.15	59.89

Properties of Orthoparadibromorthophenylenediamine. — It crystallizes from dilute alcohol in small, slender, colorless prisms, which turn dark on exposure to the air. As obtained by distillation with steam, it forms a mat of long, fine needles. It crystallizes from ligroin in radiating needles, from hot water in rhombic plates. It melts at 83° to a colorless liquid. It is freely soluble in alcohol; soluble in ether, benzene, acetone, chloroform, carbonic disulphide, or glacial acetic acid; less soluble in ligroin; slightly soluble in hot water. All its solutions turn dark on exposure to the air. It dissolves in strong, hot hydrochloric acid, forming a hydrochloride, which crystallizes out in transparent needles. Strong, hot hydrobromic acid also dissolves it and deposits a hydrobromide in short prisms. Strong nitric acid gives a red solution with it, from which nothing is precipitated on dilution, but if dilute nitric acid is used the solution has a deeper red color, and addition of water throws down an amorphous, brownish red precipitate. Cold, strong sulphuric acid dissolves it and on dilution clusters of flat, transparent prisms are deposited. Alkalies have no effect on it.

Hydrochloride of Orthoparadibromorthophenylenediamine, $C_6H_2Br_2(NH_2)NH_2Cl$.—This salt was most easily prepared by passing a stream of dry hydrochloric acid gas into a solution of the diamine in dry benzene. The hydrochloride was thrown down as a pink, gelatinous precipitate, which was dried over soft paraffin and potassic hydrate for analysis:

0.1385 gram substance gave 0.2374 gram AgBr + AgCl.

	Calculated for $C_6H_2Br_2(NH_2)_2HCl$.	Found.
Br + Cl	64.97	64.48

The pink precipitate analyzed was seen under the microscope to consist of very fine needles. It was decomposed by hot water or alkalies.

Dihydrobromide of Orthoparadibromorthophenylenediamine, $C_6H_2Br_2(NH_2Br)_2$.—When hydrobromic acid gas was passed through a solution of the diamine in dry benzene, a precipitate was obtained which probably was the dihydrobromide, but lost hydrobromic acid so easily that we were unable to get a good analysis of it. The specimens for Analyses I. and II. were dried by pressing between filter paper, III. by heating to constant weight at 95°, IV. by drying at 90° in a current of dry hydrobromic acid.

I. 0.1511 gram substance gave 0.2623 gram AgBr.
II. 0.1587 gram substance gave 0.2721 gram AgBr.
III. 0.1585 gram substance gave 0.2678 gram AgBr.
IV. 0.2672 gram substance gave 0.4498 gram AgBr.

	Calculated for $C_6H_2Br_2(NH_2)_2HBr$.	$C_6H_2Br_2(NH_2Br)_2$.	Found. I.	II.	III.	IV.
Br	69.13	74.74	73.87	72.97	71.90	71.64

The salt, therefore, loses hydrobromic acid even in an atmosphere of this gas. It is decomposed by hot water or alkalies.

Orthoparadibromorthophenylenediacetamide, $C_6H_2Br_2(NHC_2H_3O)_2$.—Half a gram of the dibromorthophenylenediamine was boiled for 15 minutes with acetic anhydride, and as the colorless solution deposited nothing on cooling, water was added, which threw down a white, flocculent precipitate. We did not succeed in finding a solvent from which this substance could be recrystallized in the ordinary way; it was, accordingly, purified by making a dilute solution in acetic acid and allowing this to stand under a bell jar, over night, with a strong solution of ammonia. As the acetic acid was neutralized by the ammonia gas, the new compound crystallized out in long needles, and two such crystallizations were sufficient for complete purification. It was dried at 95° for analysis:

0.1000 gram substance gave 0.1071 gram AgBr.

	Calculated for $C_6H_2Br_2(NHC_6H_5O)_2$.	Found.
Br	45.66	45.58

Properties.—It crystallizes in long, white needles, which melt at 227°–228°. It is soluble in ethyl or methyl alcohol, acetone, chloroform, or acetic acid; sparingly soluble in benzene or ligroin. We could not obtain crystals from any of these solutions by the usual methods. It dissolves in strong hydrochloric acid, but is precipitated on dilution; it is soluble in strong nitric acid, strong sulphuric acid, or an excess of hot sodic hydrate solution.

Orthoparadibromdiphenylenequinoxaline (*Orthoparadibromphenanthrophenazine*), $C_6H_2Br_2N_2C_2(C_6H_4)_2$.—Two-tenths gram of the dibromphenylenediamine were dissolved in alcohol and mixed with an acetic acid solution of 0.15 gram of phenanthrenequinone; a heavy precipitate, made up of fine, yellowish needles, was deposited at once, which was so pure that one recrystallization from benzene was sufficient to raise it to the constant melting point, 248°. It was dried at 95° for analysis:

0.1343 gram substance gave 0.1148 gram AgBr.

	Calculated for $C_6H_2Br_2N_2C_{14}H_8$.	Found.
Br	36.51	36.38

Properties.—It crystallizes from benzene in silky, yellow needles, arranged in radiating groups, which melt at 248°. It is soluble in hot benzene or chloroform, sparingly in cold; very slightly soluble in alcohol, ether, acetone, or glacial acetic acid; insoluble in ligroin or water. Strong hydrochloric acid turns it slightly yellow; strong nitric acid has no effect, but fuming nitric acid gives a red solution; strong sulphuric acid forms a deep red solution with it. Alkalies do not act on it.

Orthoparadibromdiphenylquinoxaline, $C_6H_2Br_2N_2C_2(C_6H_5)_2$.—A solution of 0.15 gram of benzil, in 10 cc. of alcohol, was boiled for 1 hour with 0.2 gram of the dibromphenylenediamine. As the solution cooled white needles were deposited which, after 2 recrystallizations from dilute alcohol, showed

the constant melting point 149°–150° and were dried at 95° for analysis :

0.1565 gram substance gave 0.1337 gram AgBr.

	Calculated for $C_6H_3Br_2N_5C_5(C_6H_5)_2$.	Found.
Br	36.36	36.37

Properties.—It crystallizes from dilute alcohol in long, white needles, which melt at 149°–150°. It is soluble in alcohol, ether, chloroform, benzene, acetone, hot methyl alcohol, or hot glacial acetic acid ; insoluble in ligroin or water. It is slightly soluble in strong hydrochloric acid ; hot, strong nitric acid converts it into a pale yellow solution and an oil, on dilution with water a white precipitate is formed ; cold, strong sulphuric acid forms with it a blood-red solution, from which water precipitates a white solid. Alkalies have no effect on it.

When the orthoparadibromphenylenediamine was treated with tetrabromorthobenzoquinone, a red, slightly tarry mass was formed, from which we have not succeeded in isolating any definite compound.

CAMBRIDGE, MASS.,
Sept. 12, 1905.

Contributions from the Chemical Laboratory of Harvard College.

ON CERTAIN DERIVATIVES OF TETRABROMORTHOBENZOQUINONE.[1]

BY C. LORING JACKSON AND F. W. RUSSE.

In this paper we describe a continuation of the investigation of tetrabromorthobenzoquinone, $C_6Br_4O_2$, which has been carried on for some years in this laboratory.[2]

We turned our attention in the first place to the action of ketones on tetrabromorthobenzoquinone, as preliminary experiments had shown that these substances reacted even in the cold and Japp found that acetone[3] or acetophenone[4] combines

[1] The work described in this paper formed part of a thesis presented to the Faculty of Arts and Sciences of Harvard University, for the degree of Doctor of Philosophy, by Frederick W. Russe.

[2] Jackson and Koch : THIS JOURNAL, **26**, 10 (1901). Jackson and Porter : *Ibid.*, **30**, 518 (1903) ; **31**, 89 (1904). Jackson and Carlton : *Ibid.*, **34**, 422 (1905).

[3] Japp and Streatfield : J. Chem. Soc., **41**, 274 (1882).

[4] Japp and Meldrum : *Ibid.*, **75**, 1034 (1899).

with phenanthrenequinone, while Klinger[1] has obtained addition compounds of aldehydes with it. It seemed probable, therefore, that our orthobenzoquinone would give, under these conditions, series of compounds similar to those formed by the action of alcohol on it.[2] Porter and one[3] of us, in fact, had found that acetophenone combined with tetrabromorthoquinone in the cold, forming an unstable addition product, which may be considered to be the quinone with 1 mol. of acetophenone of crystallization. On longer standing with acetophenone a yellow product was formed, the nature of which was not determined. When the substances were boiled together the bromine compounds were broken up in great measure and the hydrobromic acid formed converted part of the acetophenone into triphenylbenzene.

Of the ketones studied by us, benzophenone was the only one that did not act on tetrabromorthoquinone in the cold, and even from this we obtained an action if it was dissolved in chloroform, but we are inclined to ascribe this to the solvent, as there was no action when benzene was used. Acetone, diethylketone, mesityl oxide, or acetophenone reacted easily with the tetrabromorthobenzoquinone, but to our great disappointment, instead of forming addition compounds the same products were formed in each case. These were three in number: the red hexabromorthoquinopyrocatechin ether,[4]

$$C_6Br_4O_2.C_6Br_2O_2;$$

brown hexabromdihydroxypyrocatechin ether,[5]

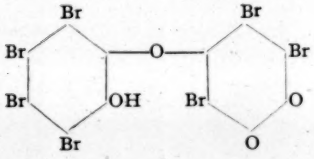
$$C_6Br_4O_2.C_6Br_2(OH)_2,$$

and a new yellow compound, identified as heptabromorthoquinopyrocatechin hemiether, $C_6Br_4(OH)OC_6Br_3O_2$. By regulating the conditions of the reaction each of these compounds can be made the principal product; thus with half its weight of acetone, best diluted with benzene, the tetrabromorthoquinone gave the heptabrom compound almost pure; with twice

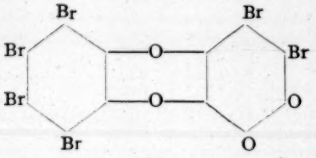
[1] Ann. Chem. (Liebig), **249**, 138 (1888).
[2] This Journal, **31**, 89 (1904).
[3] *Ibid.*, **31**, 116 (1904).
[4] *Ibid.*, **26**, 35 (1901).
[5] *Ibid.*, **26**, 38 (1901).

its weight of acetone the hexabromorthoquinopyrocatechin ether was formed at first, which on longer standing, went almost completely into the dihydroxy compound. Shining brassy scales were also observed frequently among the products of the reaction, but these, by continuous extraction with benzene, yielded the two hexabrom ethers and probably, therefore, consisted of a mixture or loose compound of these two substances.

The constitution of the heptabromorthoquinopyrocatechin hemiether, I., was determined by the following observations:[1]



I.



II.

It passed into the hexabrom ether, II., with great ease, when treated with acetone, dilute alcohol, dilute acids, or even when exposed to the air. It must contain quino oxygens, because nitric acid did not act on it, as would have been the case if it were a trihydroxy compound; and benzoyl chloride gave a derivative analyzing nearly for $C_{12}Br_7O(OCOC_6H_5)_3$, while at the same time a brown gas was given off which bleached moist litmus paper. Graebe[2] and H. Schulz[3] have shown that acetyl chloride or bromide acts on paraquinones in a similar way, giving a hydroquinone diacetate and chlorine or bromine, which

[1] A possible formula isomeric with I. is discussed later.

[2] Ann. Chem. (Liebig), 146, 13, 23 (1869).

[3] Ber. d. chem. Ges., 15, 652 (1882).

is afterward used up, more or less completely, by secondary reactions. In our case, the chlorine formed in this way displaced part of the bromine in the heptabrom compound. An experiment with tetrabromorthoquinone itself gave confirmatory results, as, when treated with benzoyl chloride, it gave a brown gas, probably a mixture of bromine and chlorine, and a product containing the percentage of Br for the formula $C_6Br_4(OCOC_6H_5)_2$, but which melted at 172°–174° instead of at 197°, the melting point of the tetrabrompyrocatechin dibenzoate, which was made for comparison. We cannot explain this difference of 25° in the melting points.

In addition to the three derivatives of the quinone already mentioned there was formed in every case a bromketone, as was unpleasantly evident by its violent action on the eyes. With acetophenone the compound formed was the ω-bromacetophenone, $C_6H_5COCH_2Br$, which we proved by converting it into ω-anilinoacetophenone, $C_6H_5COCH_2NC_6H_5$, melting at 94°.

The reaction by which the yellow hemiether was formed can be written as follows:

$$2C_6Br_4O_2 + C_6H_5COCH_2 = C_6Br_4(OH)O.C_6Br_3O_2 + C_6H_5COCH_2Br.$$

The red hexabrom ether would, later, be formed from this,

$$C_6Br_4(OH)O.C_6Br_3O_2 = C_6Br_4O_2.C_6Br_2O_2 + HBr,$$

and the brown dihydroxy ether would result from the reducing action of the hydrobromic acid:

$$C_6Br_4O_2.C_6Br_2O_2 + 2HBr = C_6Br_4O_2.C_6Br_2(OH)_2 + Br_2.$$

The free bromine would then act on the excess of the ketone to give more hydrobromic acid for this last reaction.

That the hexabromorthoquinopyrocatechin ether,

$$C_6Br_4O_2.C_6Br_2O_2,$$

could be reduced by hydrobromic acid to the dihydroxy ether, as in the last reaction, was shown by a special experiment, in which it was treated with acetone and bromine. In this work the dihydroxy body was obtained either in brown plates looking like mica, or in white, fibrous needles like asbestos, and it

was proved that the two products were identical in spite of the difference in their appearance.[1]

If bromine was added to a mixture of acetone and tetrabromorthoquinone the action seemed to be much more rapid and ran further than when acetone was used alone. This was obviously due to the reducing action of the hydrobromic acid formed, which converted part of the quinone to tetrabrompyrocatechin, and this, reacting with unaltered quinone, formed the hemiether or ether. If the mixture was diluted with benzene, the reduction ran so far that tetrabrompyrocatechin was one of the products of the reaction.

The action of tetrabromorthoquinone with oenanthol or with benzaldehyde gave the red and yellow products obtained by the action of ketones. Under these circumstances it did not seem worth while to multiply experiments with aldehydes.

In his paper[2] on tetrabromorthoquinone, Zincke mentions a black substance, which he took for the quinhydrone, but he did not study it in detail. Koch and one of us[3] did not succeed in making this compound, but we have found that it is formed whenever hot solutions of the tetrabromorthoquinone and tetrabrompyrocatechin, in equivalent amounts, are mixed and allowed to cool at once. Chloroform is the best solvent for this purpose. The shining, black crystals obtained in this way gave analytical results agreeing with the formula

$$C_6Br_4(OH)_2.C_6Br_4O_2.H_2O.$$

As this formula rests on six analyses of different specimens, there can be no doubt that the substance is not

$$C_6Br_4(OH)_2.C_6Br_4O_2.$$

That the low result was not due to a loss of hydrobromic acid was shown by a special experiment, and therefore it follows that it must be caused by the addition of some substance to the quinhydrone, which can only be water, since the same product was obtained with chloroform or benzene. Such a strong tendency to combine with water was observed by Porter and one

[1] Cf. similar observations of Shaffer.

[2] Ber. d. chem. Ges., **20**, 1778 (1887).

[3] This Journal, **26**, 37 (1901).

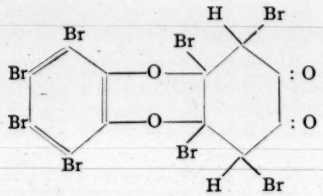
of us[1] with the tetrabromorthoquinone. An attempt to obtain a similar addition with isoamyl alcohol gave only the water compound.

A series of synthetic experiments showed that the substance contained 1 molecule of the tetrabromorthoquinone combined with 1 of tetrabrompyrocatechin. Our reasons for considering it a quinhydrone are its formation from the orthoquinone and pyrocatechin, its marked color and its composition, apart from the unexplained molecule of water. Its behavior with solvents, on the other hand, at first sight seems different from that of the paraquinhydrone, since it is converted with great ease into the heptabrompyrocatechin hemiether, $C_6Br_4(OH)O.C_6Br_3O_2$, and tetrabrompyrocatechin. It is possible, however, that this change is preceded by a dissociation into its components similar to that observed with paraquinhydrone. In the decomposition with boiling benzene the change was followed quantitatively and was found to correspond to the reaction:

$$3C_6Br_4(OH)_2.C_6Br_4O_2.H_2O = 2C_{12}Br_7O_4H + 2C_6Br_4(OH)_2 + Br_2 + 3H_2O.$$

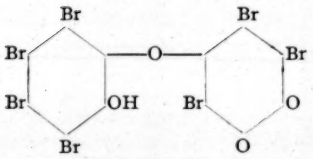
The same reaction took place when the dry quinhydrone was heated.

If, as we think, our substance is the orthoquinhydrone, it should have the graphical formula III., according to the constitution established by Posner[2] for the para compound:

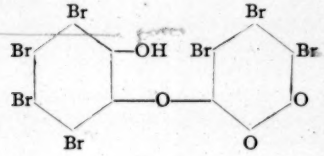


III.

[1] THIS JOURNAL, 31, 109 (1904).
[2] Ann. Chem. (Liebig), 336, 85 (1904).



I.



IV.

We give only the keto form, as it seems to us the strong color of the quinhydrones renders Posner's enol formula improbable. In this discussion we have omitted the molecule of water, as we have no experimental evidence to show how it is attached to the molecule.

If the heptabrom hemiether is formed from the undissociated quinhydrone, Formula I. must be the correct one for it, as a substance having Formula IV. could not be formed from III. without dissociation, but, as we have pointed out already, the analogy with the para compound would lead us to expect a complete dissociation of the quinhydrone in its solutions, so that this argument is entitled to but little weight.

We have devoted a great deal of time to the study of the action of acetic acid on tetrabromorthoquinone, but, although our results explain one of the reactions which takes place, they are not in harmony with those of our predecessors. Koch,[1] by the long-continued action of warm acetic acid on tetrabromorthoquinone, obtained, without difficulty, a white product melting at 230° without visible decomposition,[2] and giving

[1] THIS JOURNAL, 26, 42 (1901).

[2] This fact was verified by taking the melting point of a specimen of the substance left from Koch's work.

analytical results corresponding to the formula $C_{14}H_2Br_8O_5$. Porter,[1] who took up the work later, could not obtain this substance, but found instead a yellowish product resembling heptabromorthoquinopyrocatechin hemiether in appearance, but melting, with decomposition, at 220°–230°, instead of at 244°–245° and containing 3.5 per cent less bromine. Our attempts to prepare Koch's products were even less successful as, when we followed most carefully the directions given by him, we obtained nothing but the red hexabromorthoquinopyrocatechin ether, $C_6Br_4O_2.C_6Br_2O_2$. Three different men, therefore, have obtained three different results from the same process, showing that slight and apparently trifling differences in the conditions must have a marked effect on the product.

In other experiments the method of Koch was somewhat modified. For instance, we replaced with benzene the acetic acid or the alcohol and acetic acid used by Koch in purifying this compound and, in both cases, obtained the same substance, which crystallized in yellow needles and melted, with decomposition, between 235° and 250°. Another experiment, in which the heating of the tetrabromorthoquinone with acetic acid at 100° was continued much longer, yielded nearly pure heptabromorthoquinopyrocatechin hemiether,

$$C_6Br_4(OH)O.C_6Br_2O_2;$$

and, when the materials were boiled together for 7 hours instead of being heated only at 100°, some tetrabrompyrocatechin was detected in the product.

We have also studied the action of acetic acid on tetrabromorthoquinone in the cold. Porter obtained, in a preliminary experiment of this sort, 2 products, one white melting at 85°–90° without apparent decomposition, the other pinkish white, melting between 90° and 110°, but he made no attempt to purify either of them. In the many experiments tried by us we have found no indications of these substances, but instead have obtained only nearly square, thick, rhombic plates, which redden when heated, but do not melt under 300°. They gave results on analysis corresponding to the formula

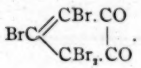
[1] THIS JOURNAL, 31, 114 (1904).

$(C_6Br_4O_2)_2.(C_2H_4O_2)_3$.

As they had no melting point, and could be recrystallized only with great difficulty, it is not certain that the specimen analyzed was pure, but it seems hardly probable that any large amount of impurity could be present in such well formed crystals.

If this substance was crystallized 10 times from benzene it was converted into the yellow needles, melting, with decomposition, at 235°–250°, obtained by the action of hot acetic acid; and the same compound was also formed by the action of formic acid on tetrabromorthoquinone. As this same product has been made by 3 methods from acetic acid and also from formic acid, we feel there is no doubt that it is a definite compound, in spite of the wide range of its decomposition temperature. Its analysis indicates that it is the ether or oxide corresponding to the heptabromorthoquinopyrocatechin hemiether, that is, $(C_6Br_4.O.C_6Br_3O_2)_2O$, and it may be called, therefore, diheptabromorthoquinopyrocatechin ether. A specimen of the substance, crystallized 12 times from benzene, seemed to be partially converted into the hemiether, $C_6Br_4(OH)O.C_6Br_3O_2$, a result in harmony with our theory of its constitution, but other confirmatory results must be discovered before the formula can be considered finally established. The action of propionic, butyric, or valerianic acids on tetrabromorthoquinone gave what seemed to be the same compound in a somewhat impure state.

Some attempts to make bromine addition products of tetrabromorthoquinone did not lead to the desired result, but in the course of this work we boiled it with fuming nitric acid and bromine and obtained 2 new compounds, a white acid soluble in water, and a yellow substance melting, without decomposition, at 142°, which gave analytical results corresponding to the formula $C_5Br_4O_2$. Upon treating this substance with orthodiamines, products were obtained which gave, with sulphuric acid, the deep red color characteristic of quinoxalines of this class. We feel justified, therefore, in considering it, for the present, the tetrabromcyclopenteneorthoquinone,



Unfortunately, this product and the white acid were discovered too late in the year for thorough study. The investigation of both will be continued in this laboratory in the coming academic year.

EXPERIMENTAL.

The tetrabromorthobenzoquinone used in this work was prepared by the method described by Koch and one of us,[1] with the improvements introduced by Shaffer,[2] except that less care was taken in cooling the oxidation mixture both before the oxidation and after the addition of water; 30 grams of tetrabrompyrocatechin yielded in this way 24 grams of the orthoquinone, melting at 149°–150°.

Action of Cold Acetone on Tetrabromorthoquinone.

Our preliminary experiments showed that there were three products of this action, a yellow, a red and a brown, any one of which could be obtained as the principal product by a careful adjustment of the conditions.

The Red Product.—The best way to obtain this substance was to allow 5 grams of tetrabromorthoquinone to stand at ordinary temperatures, in a corked flask, with 10–15 grams of pure, anhydrous acetone. During the first 4 or 5 days the product was deposited in small, red prisms, and if these were filtered out each day, the yield varied from 50 to 65 per cent of the quinone used. The yield depended on the amount of acetone, as, if the quinone was treated with half its weight of acetone, very little of the red product was formed, and with its own weight only 10–15 per cent of the weight of the quinone was obtained. The crystals as deposited from the acetone solution were often of good size, and showed the form characteristic of the hexabromorthoquinopyrocatechin ether

[1] THIS JOURNAL, 26, 34 (1901).
[2] *Ibid.*, 34, 460 (1905).

discovered by Koch and one of us.[1] That it was this compound was shown by its other properties—infusibility even at 300° and essential insolubility in all solvents except nitrobenzene—and by the following analyses of the substance made without recrystallization, which accounts for the somewhat high percentages. Each specimen used proceeded from a different preparation.

I. 0.2688 gram substance gave 0.4447 gram AgBr.
II. 0.2175 gram substance gave 0.3589 gram AgBr.
III. 0.2196 gram substance gave 0.3628 gram AgBr.

	Calculated for $C_6Br_4O_2.C_6Br_2O_2$.	Found. I.	II.	III.
Br	69.76	70.42	70.23	70.33

In this and all the actions of acetone with the quinone, bromacetone was formed as a secondary product, and to avoid its irritating effect on the eyes it must be removed by allowing the crystals to stand under a good hood before studying them.

The Brown Product.—This substance is the final product of the action of acetone on tetrabromorthoquinone. If, therefore, a mixture of 5 grams of the quinone with 10 cc. of acetone, such as that mentioned in the last section, was allowed to stand more than 5 days, the red crystals, and some glittering yellow plates, which were also formed, were converted, in a few days more, into long, brownish black needles, the solution turning from red to straw color.

The brown compound was also formed by the further action of acetone on the red hexabromorthoquinopyrocatechin ether. It is nearly insoluble in the common solvents except alcohol, in which it is very slightly soluble. From this it crystallizes in slender, white needles, which mat together like asbestos. Nitrobenzene dissolves it freely and it crystallizes from this solution in mica-like plates, apparently hexagonal in form and of a pale brown color, or, if crystallized very slowly, in white needles. It decomposes at 304°–305°. Sodic hydrate, in aqueous solution, does not dissolve it, but sometimes turns the white needles purple. These properties indicate that the sub-

[1] THIS JOURNAL, 26, 36 (1901).

stance is the hexabromdihydroxypyrocatechin ether[1] and this was confirmed by the following analysis of the substance recrystallized from nitrobenzene:

0.2669 gram substance gave 0.4370 gram AgBr.

	Calculated for $C_6Br_4O_2.C_6Br_2(OH)_2$.	Found.
Br	69.56	69.68

The glittering yellow plates mentioned above appeared almost invariably as an intermediate product in the action of acetone on tetrabromorthoquinone; they had a brassy color and luster and looked not unlike bronze powder. On treatment with benzene, in a continuous extractor, they were converted into the red and brown products described above. Longer standing with acetone changed them completely into the hexabromdihydroxypyrocatechin ether.

The Yellow Product. Heptabromorthoquinopyrocatechin Hemiether, $C_6Br_4(OH)O.C_6Br_3O_2$.—This substance was made by mixing 5 grams of tetrabromorthoquinone with 2.5 grams of acetone and allowing the damp powder to stand in a corked flask. In 24–48 hours the solid began to swell up, as lime does in slaking, and was converted into an amorphous pink mass, which, after standing another day, had crystallized in small needles and consisted principally of the yellow compound, nearly free from the brown or red substance. This product was first allowed to stand in a current of air, until the bromacetone had evaporated. It was then extracted with benzene and purified by repeated crystallization from this solvent.

An even purer product was obtained by the following method: One gram of the tetrabromorthoquinone was mixed with 0.5 gram of pure acetone, dissolved in 10 grams of benzene, and the mixture was allowed to stand at ordinary temperatures in a corked flask. For 10 days there was no sign of a reaction, but after that time the solution began to take on a straw-yellow color, and at the end of 2 weeks deposited yellow crystals, which were nearly pure. They were freed from

[1] THIS JOURNAL, 26, 39 (1901).

bromacetone and purified as before. The yield was 70 per cent of the quinone used. Most of the substance used by us was prepared by this method. A specimen recrystallized from benzene, until it showed the constant decomposition point 244°–245°, was carefully dried between filter papers for analysis:

I. 1.2158 grams substance, heated at 90°–95°, lost 0.1650 gram C_6H_6.

II. 0.5553 gram lost 0.0735 gram C_6H_6.

III. 0.5109 gram lost 0.0684 gram C_6H_6.

	Calculated for $C_6Br_4(OH)O.C_6Br_3O_2.1\frac{1}{2}C_6H_6$.	Found. I.	II.	III.
C_6H_6	13.22	13.57	13.23	13.39

I. 0.4051 gram substance, dried at 90°–95°, gave 0.2714 gram CO_2 and 0.0148 gram H_2O.

II. 0.3214 gram substance gave 0.5520 gram AgBr (Carius).

III. 0.3155 gram substance gave 0.5412 gram AgBr.

	Calculated for $C_6Br_4(OH)O.C_6Br_3O_2$.	Found. I.	II.	III.
C	18.73	18.27	. .	. .
H	0.13	0.41	. .	. .
Br	72.80	. .	73.10	73.02

Properties of Heptabromorthoquinopyrocatechin Hemiether.—Crystallized from benzene, it formed large square plates or thick, square prisms, of a full yellow color, which effloresce on exposure to the air. When heated it turns orange between 200° and 240°, and at 244°–245° melts to a deep red liquid with great increase in volume and evolution of a little reddish gas. It is soluble in hot benzene, chloroform, ether, or nitrobenzene; essentially insoluble in ligroin. Ethyl alcohol dissolves it, but if the solution is heated, even by holding the vessel in the hand, decomposition sets in as shown by the formation of a red precipitate of hexabromorthoquinopyrocatechin ether, $C_6Br_4O_2.C_6Br_2O_2$. Methyl alcohol acts in the same way, but more slowly. It is also converted into the hexabrom ether by long exposure to the air, by the action of dilute acids, by acetic anhydride, or acetyl chloride, or by standing at ordinary temperatures with acetone for a month;

in this last case the action goes further, as part of the hexabrom ether is converted into the brown hexabromdihydroxypyrocatechin ether, $C_6Br_4O_2.C_6Br_2(OH)_2$. Strong or fuming nitric acid apparently did not act on it. Sodic hydrate decomposed it, dissolving part of it and leaving the rest in the form of a black, amorphous mass.

Reduction of Heptabromorthoquinopyrocatechin Hemiether.—An attempt to reduce this substance with sodium amalgam failed, because of the formation of the black product of the action of sodic hydrate.

With zinc and dilute acetic acid a flocculent, purple-brown substance was obtained, which was recognized as hexabromdihydroxypyrocatechin ether by the following properties: It decomposed at 306°–307°; crystallized from hot alcohol, in which it was very sparingly soluble, in white, asbestos-like needles; from hot nitrobenzene in plates or needles; it was essentially insoluble in the other common solvents except benzene, in which it is slightly soluble. Benzoyl chloride converted it into a white ether. One gram of the heptabrom ether gave 0.6 gram of the hexabrom ether, or 67 per cent of the theoretical yield.

Phenylhydrazine, in benzene solution, also converted the heptabrom hemiether into the hexabromdihydroxy ether, which, in this case, appeared in pink plates looking like mica and was recognized by its properties. It was mixed with white needles of phenylhydrazine hydrobromide.

Tribenzoylheptabromdihydroxypyrocatechin Hemiether, $C_6Br_4(OCOC_6H_5)O.C_6Br_2(OCOC_6H_5)_2$.—Although acetyl chloride gave the hexabrom ether, benzoyl chloride converted the heptabromorthoquinopyrocatechin hemiether into its tribenzoyl derivative. For this purpose 4 grams of the hemiether were boiled with 10 grams of benzoyl chloride, for 1 hour. The red solution at first gave off red fumes which bleached moist litmus paper and, therefore, contained bromine, probably mixed with chlorine. After 10 or 15 minutes the evolution of these fumes ceased, and at the end of the hour the solution, on cooling, deposited a white, crystalline mass, which was washed

thoroughly with hot water to remove benzoyl chloride, and then crystallized repeatedly from benzene until it showed the constant melting point 294°–296°, when it was dried at 95° for analysis. The specimen used for the combustion was boiled a second time with benzoyl chloride and purified as before.

I. 0.3098 gram substance gave 0.4042 gram CO_2 and 0.0382 gram H_2O.

II. 0.2484 gram substance gave 0.3072 gram AgBr.

	Calculated for $C_6Br_4(OCOC_6H_5)O.C_6Br_3(OCOC_6H_5)_2$.	Found. I.	II.
C	36.56	35.58	. .
H	1.38	1.38	. .
Br	51.71	. .	52.62

These results seem to indicate that our product contained an impurity of a dibenzoyl compound, but the case is probably not so simple as this, since bromine was given off in the formation of the substance and, therefore, the chlorine set free by the action of the quinone on benzoyl chloride must have replaced the bromine in part of the hemiether, although, as the analyses show no trace of the presence of a chlorine compound, this must have been removed by the recrystallization.

Properties of the Tribenzoyl Compound.—It crystallizes from benzene in small, flat, transparent plates, which melt at 294°–296°, apparently without decomposition. This somewhat indefinite melting point is in accord with our theory that the substance was contaminated with the dibenzoyl compound. It is soluble in benzene or nitrobenzene; sparingly soluble in alcohol; essentially insoluble in ligroin or water.

Action of Benzoyl Chloride on Tetrabromorthoquinone.—Eight grams of the quinone were boiled for 2 hours with 20 grams of benzoyl chloride. The solution at first was red and gave off red vapors which bleached moist litmus paper, but after 10 minutes boiling the red vapors ceased to appear and the liquid had become colorless. Nothing separated on cooling, therefore the benzoyl chloride was distilled off with steam and the white crystalline residue, well washed with hot water, was purified by recrystallization from a mixture of 1 part of ben-

zene and 2 of ligroin until it showed the constant melting point 172°–174°, when it was dried at 95° for analysis.

0.2266 gram substance gave 0.2665 gram AgBr.

	Calculated for $C_6Br_4(OCOC_6H_5)_2$.	Found.
Br	50.47	50.05

This analysis would make the substance tetrabrompyrocatechin dibenzoate, but it melted at 172°–174°, whereas the real melting-point of this compound is 197°, as shown in the following section. This large difference in the melting point would indicate a larger amount of impurity than is shown by the analysis, so that we are unable to account for this anomaly, which is rendered still more puzzling by the facts that the melting point, 172°–174°, although not sharp, was constant and the crystals appeared homogeneous under the microscope.

Dibenzoate of Tetrabrompyrocatechin, $C_6Br_4(OCOC_6H_5)_2$.—Five grams of tetrabrompyrocatechin were heated for 7 hours with 10 grams of benzoyl chloride. The product was purified as described in the preceding section, and showed the constant melting-point 197°.

0.1814 gram substance gave 0.2153 gram AgBr.

	Calculated for $C_6Br_4(OCOC_6H_5)_2$.	Found.
Br	50.47	50.52

Properties of Tetrabrompyrocatechindibenzoate.—It crystallizes in transparent, square plates from a mixture of benzene and ligroin, and melts at 197° to a colorless liquid. It is soluble in benzene, or chloroform; slightly soluble in hot alcohol, methyl alcohol, or benzene; insoluble in ligroin.

If the tetrabrompyrocatechin was boiled gently with benzoyl chloride for only 5 or 10 minutes instead of several hours, a different product was obtained, which, after the usual purification, melted at 215°–216° and, judging from a single analysis, was an impure monobenzoate of tetrabrompyrocatechin, as this would contain 60.36 per cent of bromine and we found 63.36 per cent. It crystallized from hot benzene in long, white needles. The substance was not of sufficient importance to make it worth while to prepare it in a state of purity.

Action of Hot Acetone.—One gram of tetrabromorthoquinone, dissolved in 1 gram of hot acetone, was heated for an hour on the steam-bath. The only solid product seemed to be the brilliant red hexabromorthoquinopyrocatechin ether. The vapor from the acetone was exceedingly irritating to the eyes and on adding water a heavy, dark colored oil, probably bromacetone, was precipitated.

Action of Acetophenone on Tetrabromorthoquinone.—In our experiments on the action of cold acetophenone on tetrabromorthoquinone we used either equal weights of the two substances or twice as much of the ketone as of the quinone. During the second and third days of standing red crystals of the quinone with acetophenone of crystallization[1] were deposited, but on longer standing they redissolved, and at the end of a week red and yellow crystals appeared, which, after a month, were followed by brown needles. These three products proved to be the same as those formed with acetone, that is $C_6Br_4O_2.C_6Br_2O_2$, $C_6Br_4O_2.C_6Br_3(OH)$, and $C_6Br_4(OH)O.C_6Br_3O_2$, of which the last is formed in by far the largest quantity and, if the acetophenone is diluted with benzene, this seems to be the only aromatic product of the reaction, as was the case with acetone. After these products began to form the vapors from the solution became very irritating to the eyes, though not so much so as in the case of acetone, which is undoubtedly due to the slighter volatility of the acetophenone derivative. In order to determine the nature of this irritating substance, part of the filtrate from a mixture, which had deposited crystals of heptabromorthoquinopyrocatechin hemiether, was allowed to evaporate spontaneously; the residue consisted of crystals which melted, in the crude state, at 45°–48°, whereas the ω-bromacetophenone melts at 50°. The rest of the filtrate was mixed with 4 volumes of aniline and 4 of alcohol and allowed to stand over night, when it deposited long, yellow needles which, after recrystallization from alcohol, melted at 94° (the melting point of ω-acetophenoneanilid is 93°). It follows, therefore, that the irritating substance was ω-bromacetophenone, $C_6H_5COCH_2Br$.

[1] Jackson and Porter: THIS JOURNAL, 31, 116 (1904).

When 1 gram of diethylketone was allowed to stand with 1 gram of the quinone, the red product appeared in 2 days, the yellow in 6, and the brown needles in 10. When the mixture was diluted with benzene, the yellow body alone was formed in 20 days. Mesityl oxide, with half its weight of the quinone, gave the red crystals with some of the yellow product in 6 days, and on longer standing a blackish brown mass. With benzene the yellow product was formed after 2 weeks.

Benzophenone, allowed to stand with its own weight of tetrabromorthoquinone, at 70°–80°, gave no crystalline product even after 3 months, and the same negative result was obtained when the mixture was dissolved in benzene; when 1 gram of each was dissolved in five grams of chloroform, 0.5 gram of heptabromorthoquinopyrocatechin hemiether was obtained after 3 months. This result, however, we think was due to the action of the chloroform rather than to that of the benzophenone.

Action of Bromine and Acetone upon the Tetrabromorthoquinone.—The following experiments throw some light on the nature of the reaction. One gram of tetrabromorthoquinone mixed with 0.5 gram of acetone and 2 drops of bromine, after standing over night, was converted completely into the red and yellow products mixed with a little of the brown. A similar experiment without bromine (5 grams of quinone with 2.5 grams acetone) did not act for 24 hours, and the action was complete only in 60 hours, the product being principally the yellow compound.

A solution of 1 gram of the quinone in 5 grams of benzene, with 0.5 gram acetone and 3 drops of bromine, changed color in 1 night from red to straw-yellow, and left, on evaporation, crystals of the yellow product with white needles melting at 188°–190°, which gave a yellow solution with sodic hydrate and a red product with nitric acid; they were, therefore, tetrabrompyrocatechin (melting point 187°, Stenhouse; 192°–193°, Zincke). In the corresponding experiment without bromine, using 10 grams of benzene instead of 5 grams, the reaction did not begin until the mixture had stood 10 days, and was

complete in a fortnight, the product being the heptabromorthoquinopyrocatechin hemiether with no tetrabrompyrocatechin. It is evident, from these experiments, that the reactions run much more rapidly and further in presence of bromine than without it, which we ascribe to the reducing action of the hydrobromic acid formed in large quantity by the action of the bromine on the acetone.

Corresponding experiments with hexabromorthoquinopyrocatechin ether first made plain the properties of the dihydroxy compound formed from it by reduction, and thus enabled us to recognize as this body the blackish-brown product of the action of acetone on tetrabromorthoquinone. Two grams of the red hexabrom ether were mixed with 30 grams of acetone and 3 grams of bromine, and shaken until the reaction had taken place. If the shaking was omitted the ether collected in lumps, and the reagents then acted only superficially and, therefore, incompletely. After half an hour the red ether was converted entirely either into white, fibrous needles, or brown plates like mica, the yield in either case being 90 per cent of the red ether taken. In spite of many experiments we have not succeeded in determining the conditions which favored the formation of either of these products, except that the needles seemed to be more commonly formed when the proportion of acetone was large.

The two products, in spite of the difference in their appearance, proved to be identical. If recrystallized from alcohol, in which they are sparingly soluble, the white needles matting together like asbestos were obtained. If crystallized from nitrobenzene, each gave the brown plates like mica. Both decomposed at 306°–307°, and gave the following results on analysis, in which I. was a specimen of the brown plates, and II. of the white needles, each recrystallized from nitrobenzene, and dried at 95°.

I. 0.1537 gram of substance gave 0.2526 gram AgBr.
II. 0.1226 gram substance gave 0.2006 gram AgBr.

	Calculated for $C_6Br_4O_2.C_6Br_3(OH)_2$.	Found. I.	II.
Br	69.56	69.93	69.63

For still greater certainty it was converted into the monobenzoyl ester by the action of benzoyl chloride.

0.1199 gram substance gave 0.1714 gram AgBr.

	Calculated for $C_6Br_4O_2.C_6Br_2(OH)OCOC_6H_5$.	Found.
Br	60.45	60.82

Action of Aldehyds on Tetrabromorthoquinone.—Only two aldehyds were tried, oenanthol as a fat aldehyd and benzaldehyd to represent the aromatic series. As they gave essentially the same results as the ketones, we thought it not worth while to multiply experiments.

One gram of the quinone, after standing for 2 days with 2.5 grams of oenanthol, deposited red and yellow crystals of hexabromorthoquinopyrocatechin ether and heptabromorthoquinopyrocatechin hemiether, and after 6 days the whole of the quinone had been converted into these products. One gram of the quinone with 0.5 gram of oenanthol and 5 grams of benzene gave, after 20 days, the yellow product unmixed with any of the red.

One gram of the tetrabromorthoquinone stood with 2 grams of benzaldehyd. After 3 days the red color of the solution changed to straw-yellow, and the crystals of benzoic acid formed were colored yellow. After removing the benzoic acid with hot water, a mixture of the yellow and red products so often mentioned was obtained. The brown product was not obtained from either aldehyd, but probably would have been formed if the action had continued longer.

Octobromorthoquinhydrone, $C_6Br_4O_2.C_6Br_4(OH)_2.H_2O$. — This substance was prepared by Zincke,[1] but not analyzed or studied by him. He made it by mixing equal parts of tetrabrompyrocatechin and tetrabromorthoquinone, dissolved in benzene or ether. Our preliminary experiments showed that chloroform gave a better result than either of these solvents, as the product is so soluble in ether that it can be obtained only by evaporation, which is always accompanied by partial decomposition, while benzene converts it into heptabromorthoquinopyrocatechin hemiether so quickly that good results can be obtained

[1] Ber. d. chem. Ges., **20**, 1778 (1887).

only by very rapid work. Chloroform, on the other hand, gave the substance in a pure state, without difficulty, by the following process: Equal parts of tetrabromorthoquinone and tetrabrompyrocatechin were dissolved, separately, in the least possible quantity of hot chloroform, the solutions mixed and immediately cooled, when long black crystals were deposited, which, after pressing between filter paper, were dried *in vacuo* for analysis. Analyses I., II., III. and IV. That the solvent did not influence the nature of the product is shown by Analyses V., and VI. which were made with specimens prepared from hot benzene, to which its own volume of ligroin had been added before cooling.

I. 0.6553 gram of substance gave 0.3982 gram CO_2 and 0.0454 gram H_2O.

II. 0.3194 gram substance gave 0.5560 gram AgBr.

III. 0.1817 gram gave 0.3161 gram AgBr.

IV. 0.2405 gram gave 0.4183 gram AgBr.

V. 0.2410 gram gave 0.4169 gram AgBr.

VI. 0.2736 gram gave 0.4737 gram AgBr.

	Calculated for $C_{12}Br_8O_4H_2.H_2O$.	Found. I.	II.	III.	IV.	V.	VI.
C	16.60	16.58	. .	. .	. .	. .	. .
H	0.46	0.78	. .	. .	. .	. .	. .
Br	73.70	. .	74.08	74.04	74.03	73.62	73.69

The substance, therefore, is not the expected quinhydrone which requires 16.94 C, and 75.40 Br, but this substance combined with 1 molecule of water. We were led to this conclusion by the following considerations: The anomalous results given above were not caused by impurities in the tetrabromorthoquinone or tetrabrompyrocatechin used, since analyses of these compounds showed they were pure. The low result on the bromine was not due to a loss of hydrobromic acid, or bromine, since we passed air for 15 minutes through a boiling benzene solution of equal parts of tetrabromorthoquinone and tetrabrompyrocatechin, during which time the air gave no reaction with moist litmus paper and no precipitate with a solution of argentic nitrate, whereas, in the formation of the quinhydrone, the solutions were not boiling for more than 1 minute.

If the experiment described above was continued for more than 15 minutes hydrobromic acid was given off, but its evolution was accompanied by the formation of heptabrompyrocatechin hemiether. As there was no loss of bromine or hydrobromic acid in the formation of the quinhydrone, the low results in the analyses must be due to the addition of some substance, and as the same product was obtained from chloroform and benzene solutions, this substance must be water. Such an addition of water is not without analogy, as Porter and one of us[1] obtained a water compound, $(C_6Br_4O_2)_2.H_2O$, by the action of ordinary benzene or toluene on tetrabromorthoquinone.

In the hope that a mixture of chloroform and an alcohol might cause the addition of the alcohol instead of water, a new specimen of the quinhydrone was made with a washed sample of chloroform, dried over calcic chloride and then mixed with 5 per cent of isoamyl alcohol. This gave the following result:

0.3142 gram substance gave 0.5469 gram AgBr.

	Calculated for $C_{12}Br_8O_4H_2.H_2O$.	Found.
Br	73.70	74.08

This specimen, therefore, has also taken up water and we can infer from this experiment that the quinhydrone has little or no tendency to combine with alcohols.

The analytical results given above cannot show in what proportion the two constituents exist in the quinhydrone; this was done, therefore, by the following synthetic experiments:

1. Two grams of tetrabromorthoquinone and 2 grams of tetrabrompyrocatechin were dissolved in 10 grams of hot chloroform, mixed and cooled. Nearly 2 grams of the black quinhydrone crystals were deposited and the mother liquor, when evaporated by a stream of dry air, gave only black crystals with no sign of either of the components.

2. Two grams of the quinone and 1 gram of the pyrocatechin, treated in the same way, gave 1 gram of black quinhydrone crystals and the mother liquor, on evaporation, showed that an excess of the quinone was present.

3. Two grams of the quinone with 4 grams of the pyro-

[1] THIS JOURNAL, 31, 109 (1904).

catechin gave 3 grams of quinhydrone crystals and the mother liquor contained an excess of the pyrocatechin.

These experiments show that 1 molecule of the tetrabrompyrocatechin combines with 1 molecule of the tetrabromorthoquinone to form the quinhydrone, which, therefore, has the formula $C_6Br_4O_2.C_6Br_4O_2H_2.H_2O$ assigned to it earlier.

Properties of the Octobromorthoquinhydrone.—It is deposited from its hot solution in chloroform in shining black needles, or slender prisms, sharply pointed at one end and often more than 1 cm. long. When heated to 110° it turns brown without melting, and it was found that this change of color was attended with a loss in weight.

1.4877 grams substance, heated to 110° for 6 hours, lost 0.1050 gram.

	Calculated.	Found.
$Br + H_2O$	8.22	7.05

The brownish red residue, on crystallization from benzene, was found to contain heptabromorthoquinopyrocatechin hemiether, $C_6Br_4(OH)O.C_6Br_3O_2$, and tetrabrompyrocatechin. The most probable reaction for the formation of these two substances would be

$$3C_6Br_4(OH)_2.C_6Br_4O_2.H_2O = 2C_{12}Br_7O_4H + 2C_6Br_4(OH)_2 + Br_2 + 3H_2O.$$

The loss of $Br_2 + H_2O$ calculated for this reaction is given under the head "calculated" above, and agrees perhaps as well as could be expected with the amount found.

The quinhydrone is freely soluble in ether; soluble in cold chloroform, more soluble in hot; rather more soluble in benzene than in chloroform; slightly soluble in ligroin; insoluble in water. Of all these solvents chloroform is the best, as the substance can be recrystallized from it, if the work is carried on quickly enough, although by long standing with chloroform the quinhydrone is converted into heptabromorthoquinopyrocatechin hemiether and tetrabrompyrocatechin. This change takes place much more rapidly in benzene solution, so that it is hard to get crystals of quinhydrone, free from these

impurities, when benzene is used in its preparation. Cold benzene brings about the change in 2 or 3 weeks, but with boiling benzene it was found to be complete in 3 hours.

To study this reaction more carefully 2 grams of tetrabromorthoquinone and 2 grams of tetrabrompyrocatechin were boiled for 5 hours, with 10 grams of benzene, when, on evaporating off the solvent, good crystals of the hemiether and of tetrabrompyrocatechin were obtained. To determine the amount of each the residue was boiled with dilute alcohol for 1 hour, which converted the hemiether completely into the insoluble hexabromorthoquinopyrocatechin ether,

$$C_6Br_4O_2.C_6Br_2O_2.$$

This was filtered out and found to weigh 2 grams; and upon adding water to the filtrate, 1.5 grams of tetrabrompyrocatechin were obtained. The reaction given earlier,

$$3C_6Br_4(OH)_2.C_6Br_2O_2.H_2O = 2C_{12}Br_6O_4H + 2C_6Br_4(OH)_2 + Br_2 + 3H_2O,$$

followed by the conversion of the hemiether into the complete ether, $C_6Br_4O_2.C_6Br_2O_2$, requires 2.11 grams of this from 4 grams of the quinhydrone and 1.31 grams of tetrabrompyrocatechin: our numbers (2 grams and 1.5 grams) are as near as we could expect with the rough methods of determination used.

When hot alcohol is used as a solvent for the quinhydrone, the decomposition goes to the formation of the red hexabrom ether mentioned above. If the quinhydrone was allowed to stand with alcohol in the cold, small red needles were obtained, probably the compound $(C_6Br_4O_2)_2.C_2H_5OH$, colored red by the hexabrom ether. Methyl alcohol, propyl alcohol, or isopropyl alcohol gave yellow or white crystals under these conditions, which were not examined, as they were supposed to be impure specimens of the corresponding α-bodies.

The quinhydrone was not reduced by aqueous sulphurous acid, probably on account of its insolubility in water, but by passing sulphurous dioxide into a solution of it in ordinary benzene, tetrabrompyrocatechin was obtained. When the

quinhydrone was boiled for 15 minutes with acetic anhydride, the deep red color of the solution gradually turned to light yellow and the product, after boiling with water and recrystallization from benzene, showed the constant melting point 214° and was, therefore, the diacetate of tetrabrompyrocatechin.

Tetrabrompyrocatechin Diacetate, $C_6Br_4O_2(C_2H_3O)_2$. — This substance was made as follows, for comparison with products from other reactions: Five grams of tetrabrompyrocatechin were boiled for 1 hour, with 15 grams of acetic anhydride. On cooling, large colorless plates were deposited, which were purified by recrystallization from benzene till they showed the constant melting point 215°–216°, when they were dried at 95° for analysis:

0.2711 gram substance gave 0.4024 gram AgBr.

	Calculated for $C_6Br_4(OC_2H_3O)_2$.	Found.
Br	62.73	63.18

Properties.—It crystallizes from benzene in colorless, square plates, which melt at 215°–216° to a colorless liquid. It is soluble in chloroform whether cold or hot; slightly soluble in alcohol, benzene, or ether when cold, soluble in these solvents when hot; essentially insoluble in water or ligroin.

Tetrabromorthoquinone and Organic Acids.—In taking up this puzzling subject we tried first to obtain from the action of warm acetic acid on tetrabromorthoquinone Koch's[1] white product, $C_{14}H_2Br_8O_5$, which melts at 230° to a colorless liquid, a fact which we confirmed with a specimen left from his research. Porter,[2] who repeated Koch's process as nearly as possible, obtained yellowish white, efflorescent, rectangular plates or prisms, melting, to a red liquid, at 220°–230°, and containing over 2 per cent less bromine. In addition to many unsuccessful preliminary experiments, we tried two on a large scale in which the utmost care was taken to have the conditions the same as those used by Koch, but in each case the whole white crude product was converted into the red hexabromorthoquinopyrocatechin ether during the crystallization.

[1] THIS JOURNAL, **26**, 42 (1901).
[2] *Ibid.*, **31**, 114 (1904).

Accordingly, in a third experiment, we changed the method of purification, which consisted, according to Koch, in extracting the crude product with 200 cc. of hot alcohol, filtering hot, and, after it had cooled, filtering again; then the filtrate was diluted with 200 cc. of water, and the white precipitate recrystallized from glacial acetic acid, until it showed the constant melting point 230°. We now recrystallized the white precipitate, thrown down by water, from benzene instead of acetic acid, and obtained long, yellow needles which decomposed, with reddening, at 235°–250°, Analysis I. In a fourth experiment the crude product was purified only by crystallization from benzene, without the use of alcohol or acetic acid. The substance obtained in this way also crystallized in long, yellow needles, and decomposed, with reddening, at 235°–250°. Analysis II.

I. 0.2430 gram substance gave 0.4202 gram AgBr.

II. 0.1806 gram substance gave 0.3102 gram AgBr.

	Found.	
	I.	II.
Br	73.58	73.11

These results show that the two products are the same, but different from that of Koch (71.45 per cent Br) or of Porter (69.26 per cent Br). The nature of our compound will be discussed later, after we have described other ways in which it was obtained.

The following experiments, in which the conditions of the reaction were somewhat varied, gave different results. Ten grams of tetrabromorthoquinone were dissolved in 20 grams of acetic acid, and heated in an Erlenmeyer flask, on the steam-bath, until all the acid had evaporated; the product was essentially pure heptabromorthoquinopyrocatechin hemiether, which was produced by the longer action of the warm acetic acid during its evaporation from the Erlenmeyer flask instead of the evaporating dish used in the earlier experiments. Five grams of the quinone were boiled, for 7 hours, with 15 grams of acetic acid; the solution, on evaporation, yielded a yellow mass containing white needles of tetrabrompyrocatechin. The more complete reduction in this case was evidently due to

the higher temperature at which the reaction took place, 118° instead of 100°.

We also studied the action of cold acetic acid on tetrabromorthoquinone. Ten grams of it were allowed to stand in a corked flask, at ordinary temperature, with 20 grams of glacial acetic acid. In 2 weeks thick prisms had formed, some of which were yellow, others red, but we do not think these were the two products of Porter,[1] as the yellow prisms were evidently the final product about to be described, and the red looked like tetrabromorthoquinone crystallized from acetic acid. After standing for 2 months only one substance remained which crystallized in well characterized, light yellow, thick prisms or rhombic plates. We have repeated this experiment 12 times, and in each case obtained this product and no other. Some of it was recrystallized from glacial acetic acid, and dried at about 50° for analysis, during which drying it lost no weight.

I. 0.3466 gram of substance gave 0.2716 gram CO_2 and 0.0426 gram H_2O.

II. 0.2491 gram of substance gave 0.3583 gram AgBr.

III. 0.2915 gram of substance gave 0.4198 gram AgBr.

	Calculated for $(C_6Br_4O_2)_2.(C_2H_4O_2)_3$.	Found. I.	II.	III.
C	21.02	21.37	. .	. .
H	1.17	1.37	. .	. .
Br	62.24	. .	61.22	61.30

The results agree better with the formula given than with any other we could find. As it did not melt, we had no criterion of purity for it, but the large homogeneous crystals indicate that it was not very impure, and the fact that we obtained it from 12 different preparations is good evidence that it is a definite compound. Many attempts were made to determine the amount of acetic acid contained in the substance by titration with a sodic hydrate solution, but no constant results were obtained in water, alcohol or benzene. The numbers varied between 19 and 24 per cent, whereas the formula given above requires 17.51 per cent.

[1] See the introduction.

Properties.—The addition compound of tetrabromorthoquinone and acetic acid crystallizes in nearly square, white, rhombic plates from glacial acetic acid. As obtained at first it frequently forms thick, square prisms of a pale yellow color. It does not melt under 300°, but gradually turns red when heated, although stable at 50°. It is soluble in alcohol, ether, benzene, or chloroform; very slightly soluble in cold acetic acid, moderately soluble in it when hot; insoluble in water, or ligroin. Strong nitric acid does not act on it. Sodic hydrate, in aqueous solution, turns it white, but does not dissolve it. As stated already, part of the sodic hydrate is neutralized by the action of this body upon it. As we thought it might be an α-body, we tried the various methods for converting an α- into a β-body, but boiling with acetic acid, heating with acetic anhydride and sodic acetate, or boiling with dilute sodic hydrate brought about no such conversion.

Crystallization from benzene decomposed the addition compound $(C_6Br_4O_2)_2.(C_2H_4O_2)_3$ as shown by the following bromine determinations: The original substance, 61.30 per cent; after 1 crystallization, 70.52 per cent; after 4, 71.73 per cent; after 10 crystallizations, 73.16 per cent. This final product is evidently identical with the substances obtained by the action of warm acetic acid followed by crystallization from benzene, which contained 73.58 and 73.11 per cent of bromine, since all of them consist of long, yellow needles, decomposing at 235°–250°. It gave the following results on analysis, but there is some doubt whether the specimen analyzed for C and H had been recrystallized as often as that used for Br.

I. 0.3088 gram substance gave 0.2194 gram CO_2 and 0.0137 gram H_2O.

II. 0.2872 gram substance gave 0.4937 gram AgBr.

	Found.	
	I.	II.
C	19.37	.
H	0.50	. .
Br	. .	73.16

As the same compound was obtained with formic acid, the

discussion of its formula is given after all the analytical data have been presented.

Action of Other Organic Acids with Tetrabromorthoquinone.—If the quinone was warmed with formic acid, in an Erlenmeyer flask, on the steam-bath, in about 15 minutes it was converted into heptabromorthoquinopyrocatechin hemiether.

Two grams of the quinone, mixed with 10 grams of formic acid, were allowed to stand, at ordinary temperatures, in a corked flask. In 4 days yellow crystals were deposited from the red solution; in 10 days the solution itself had turned yellow. The product was recrystallized 3 times from benzene, which did not alter its decomposition point, 232°–234°. In appearance and properties it resembled the products obtained from acetic acid after crystallization from benzene, and the analyses showed they were the same.

I. 0.2545 gram substance gave 0.1783 gram CO_2 and 0.0110 gram H_2O.

II. 0.2716 gram substance gave 0.4717 gram AgBr.

III. 0.3186 gram substance gave 0.5525 gram AgBr.

	Found.		
	I.	II.	III.
C	19.11	.	. .
H	0.48	. .	. .
Br	. .	73.91	73.81

Analysis II. was made with a specimen from a different preparation from that used for I. and III. As this substance has been obtained also by 3 somewhat different methods with acetic acid, there can be little doubt that it is a definite compound. Its percentage composition agrees well with that for the ether or oxide corresponding to the heptabromorthopyrocatechin hemiether.

	Calculated for $(C_6Br_4O.C_6Br_3O_2)_2O$.	Found.				
		Formic acid.		Acetic acid.		
C	18.95	19.11		19.37		
H	0.00	0.48		0.50		
Br	73.69	73.81	73.91	73.16	73.58	73.11

It may, therefore, be called diheptabromorthoquinopyrocatechin ether, but more experimental work is necessary be-

fore this formula can be considered definitely established. The only confirmatory work done by us consisted in recrystallizing a specimen, made with acetic acid, from benzene 12 times, when it seemed to be partially converted into the heptabromorthoquinopyrocatechin hemiether, $C_6Br_4(OH)O.C_6Br_3O_2$, a result in harmony with the formula proposed above.

Properties of Diheptabromorthoquinopyrocatechin Ether.—It crystallizes from benzene in long, yellow needles, which turn white on long exposure to the air, but this change is not associated with any change in the decomposition point. If recrystallized from benzene, the white crystals become yellow again. When heated very rapidly from temperatures above 200° it melts, with reddening, between 235°–250°; 232°–234° was the most definite temperature observed, but, if heated slowly, it turns red without melting. Its solution in ether or alcohol yields white crystals, although alcohol sometimes converts it into a brilliant red substance, probably the hexabromorthoquinopyrocatechin ether; a solution in benzene or carbonic disulphide gives yellow needles. Aqueous sodic hydrate darkens it.

Propionic acid, butyric acid, or isovalerianic acid gave, with the quinone in the cold, yellow crystals, apparently the same as those obtained from formic acid, but the following analyses, made after crystallization from benzene, indicate that these products, if the same, are somewhat impure:

	Butyric acid.	Isovalerianic acid.	
C	20.03	20.88	20.47
H	0.42	0.37	0.63
Br	72.36	72.36	. .

Five grams of the quinone, heated on the steam-bath with 10 grams of propionic acid, after 2 days became yellowish red, and deposited a mixture of the heptabrom hemiether,

$$C_6Br_4(OH)O.C_6Br_3O_2,$$

and unaltered tetrabromorthoquinone.

Action of Bromine and Nitric Acid on Tetrabromorthoquinone.—The experiments described in this section were undertaken in the hope of making an addition compound of tetrabrom-

orthoquinone with bromine similar to those obtained from paraquinones by Nef,[1] and we had good hope of success because Zincke and Küster[2] have made a hexachlororthobenzoquinone, but none of our experiments gave any indication of the formation of such a compound. Bromine, in chloroform solution, had no action, even when boiled for 7 hours, or exposed to sunlight 6 days.

In one experiment, to be sure, the quinone with chloroform and bromine, heated to 100°, in a sealed tube, 4 hours, gave a new substance, which, however, seemed to be the yellow product described later and, therefore, not a bromide.

When tetrabromorthoquinone was heated with a mixture of fuming nitric acid and bromine, 2 new compounds were formed. The following conditions gave good results: Ten grams of tetrabromorthoquinone were mixed with 50 cc. of fuming nitric acid and 5 cc. of bromine and the mixture heated in an Erlenmeyer flask, on the steam-bath, until the bromine had volatilized. On cooling, large yellow plates of the first compound separated, which were recrystallized from a mixture of 1 part of benzene and 1 of ligroin, until they showed the constant melting point, 142°. If the heating was continued longer another compound was formed, which was white and soluble in water and could, therefore, be easily separated from the insoluble, yellow product by washing. The same substances were obtained by the action of fuming nitric acid alone on the tetrabromorthoquinone, the necessary bromine being furnished by the decomposition of part of the quinone, but the yield in this case was even smaller than when nitric acid and bromine were used. In any case the yield left much to be desired, as most of the quinone was oxidized completely, and too long boiling destroyed both of the products.

The Yellow Product.—The substance, purified as described above, was dried at 100° for analysis:

I. 0.3286 gram substance gave 0.1828 gram CO_2 and 0.0104 gram H_2O.

[1] J. prakt. Chem., [2], **42**, 182 (1890).
[2] Ber. d. chem. Ges., **22**, 486 (1889).

II. 0.3232 gram substance gave 0.1710 gram CO_2 and 0.0055 gram H_2O.

III. 0.2043 gram substance gave 0.3729 gram AgBr.

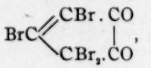
IV. 0.2761 gram substance gave 0.5041 gram AgBr.

	Calculated for $C_5Br_4O_2$.	Found. I.	II.	III.	IV.
C	14.57	15.17	14.43	. .	. .
H	0.00	0.35	0.19	. .	. .
Br	77.67	. .	.	77.67	77.69

The substance, therefore, is probably the tetrabromcyclopenteneorthoquinone, and we have adopted this constitution, provisionally, for it, as in harmony with all our observations, but, unfortunately, it was discovered so late in the year that we are unable to furnish a certain proof of its structure.

Properties of the Tetrabromcyclopenteneorthoquinone—It crystallizes from fuming nitric acid in thick plates, from a mixture of benzene and ligroin in large prisms which are, apparently, monoclinic. Its color is a full yellow, like that of potassic chromate. It melts at 142° with no signs of decomposition, and is soluble in alcohol, ether, chloroform, benzene, or acetone; slightly soluble in ligroin; insoluble in water. An aqueous solution of sodic hydrate has no effect on it in the cold, but if warmed decomposes the compound with formation of hypobromous acid, to judge by the smell. Sodic alcoholate converts it into a red substance even in the cold.

The compound was supposed to be the tetrabromcyclopenteneorthoquinone,



for the following reasons: With orthophenylenediamine it gave a brown, amorphous compound, which we could not succeed in crystallizing, so it was not analyzed, but with cold sulphuric acid it gave the dark red color characteristic of diphenylenequinoxaline. When it was boiled for an hour with an equivalent amount of 3,5-dibrom-1,2-phenylenediamine and 20 times its weight of alcohol, the dark solution deposited

small, colorless needles in moderate amount, which were dissolved in absolute alcohol, precipitated with water and crystallized once from absolute alcohol. The dark colored crystals were barely enough for analysis.

0.0644 gram substance gave 0.0963 gram AgBr.

	Calculated for $C_4Br_2(N_2C_6H_3Br_2)_2$.	Found.
Br	64.51	63.63

Little weight can be given to this analysis, owing to the small amount of substance used and the fact that there was no criterion of purity, as it blackened, without melting, at 308°. On the other hand, the fact that this substance also gave a red color with strong sulphuric acid tells in favor of the formula ascribed to it above. The yellow substance oxidized dimethylaniline in the cold, which also would indicate that it is a quinone. We hope that the study of the substance in this laboratory during the next academic year will determine its constitution with certainty.

The White Product of the Action of Nitric Acid and Bromine on Tetrabromorthoquinone.—This substance was formed by the longer action of the reagents, but we are not yet clear whether it is produced from the yellow body or at the same time with it. The compound crystallizes in white needles, which melt at 144°–146°, are very soluble in water, and give an acid reaction. It was discovered so late in the year that we were unable to study it properly, so that several analyses of the acid and its silver salt gave discordant results, showing that the substances had not been thoroughly purified. At first sight it showed some resemblance to dibrommalonic acid, which melts at 147°, with evolution of carbonic dioxide[1], and is converted into dibromacetic acid by heating it with water to 50°–60°; our compound melted at 144°–146° with partial decomposition, and gave off carbonic dioxide, when boiled with water, but the aniline salt of our acid melted at 150°–152°, whereas the dibrommalonate of aniline melts at 113°. The facts collected so far, by us, therefore, indicate that the acid is a new com-

[1] Conrad and Reinbach: Ber. d. chem. Ges., **35**, 1817 (1902). Willstätter: *Ibid.*, **35**, 1376 (1902).

pound. Its study will be continued in this laboratory in the following year.

Action of Orthodiamines on Tetrabromorthoquinone.—In the hope of obtaining a quinoxaline from tetrabromorthoquinone its action with orthophenylenediamine was studied, but the product, in every case, was a dark red, amorphous substance, which we took to be an oxidation product of the orthophenylenediamine, as, apparently, the same product was formed by the action of bromine. The reaction with the quinone was tried in acetic acid, alcohol, ether, or benzene with the same result.

As we thought that a brom derivative of the diamine might act to better advantage, we prepared the orthoparadibromorthophenylenediamine, which is described in the preceding paper, but this gave a similar result.

Potassic phenylate, or sodic alcoholates gave, with tetrabromorthoquinone, brown or red amorphous products, which we have not succeeded in purifying.

CAMBRIDGE, MASS.,
Sept. 12, 1905.

REPORTS.

Colloidal Solutions of Metals in Organic Solvents.

Svedberg, of the University of Upsala, describes, in a recent article,[1] methods of obtaining "organosols," *i. e.*, colloidal solutions of metals in organic solvents, "hydrosols" being colloid solutions in water.

Bredig,[2] and late Billitzee,[3] modifying Bredig's method, has prepared hydrosols of several metals by the action of the electric arc on the metal in water, the metal passing at the cathode into a finely diffused state.

Blake[4] placed two silver electrodes in alcohol and, with a tension of 110 volts, obtained a black alcohol without spark phenomena. Svedberg repeats and confirms Blake's work and finds the method suited to methyl alcohol also, but inapplicable to other solvents with silver electrodes, while amalgamated

[1] Ber. d. chem. Ges., **38**, 3616 (1905).
[2] Z. Chem., 1898, 951. Z. physik. Chem., **32**, 127.
[3] Ber. d. chem. Ges., **35**, 1929, 1935.
[4] Am. J. Sci., **16**, 431.

zinc electrodes remain intact even in ethyl alcohol. Svedberg then applied Bredig's method to organic solvents, but found that the solvent decomposed, with separation of carbon and other undesirable reactions, if the current was strong enough to cause cathode diffusion of the metal.

Finally, he succeeded in working out two methods. In the first the metal, in the form of sheets of thin foil, is suspended in the solvent; the electrodes are of metals not easily diffused, such as iron and aluminium; the difference of potential is 110 volts. With an intense development of sparks on the very large surface of the foil, the metal diffuses, while the current is so small that it can scarcely be measured by an ammeter. This is the essential of both of Svedberg's methods: high voltage, very low current. By this method he has obtained organosols of tin, gold, silver and lead in different solvents. The method fails, however, with metals like aluminium and iron, which resist cathode diffusion. With aluminium foil he obtained spark phenomena but no colloid.

His second method was devised to overcome this difficulty, by using a still higher potential, while keeping the current low to avoid decomposition of the solvent. Using an induction coil of 12 cm. spark length, he put in a glass condenser of 225 cm.^{2} surface, parallel to the secondary of the coil, and led the secondary poles to electrodes which dipped into the solvent in a porcelain dish. The metal was used either in granular form or in pieces of wire. On closing the circuit there is a vigorous sparking between the metal particles, the solvent at once darkens and, in a few minutes, a dark colored organosol is formed. It is, of course, better to use electrodes of the metal which is reacting, but he finds, experimentally, that the influence of the electrodes is very slight. By this method Svedberg has prepared a series of new colloids, comprising magnesium, zinc, aluminium, tin, antimony, iron, nickel, sodium and potassium.

While hydrosols of copper, copper-zinc, silver, gold, lead and bismuth have been made by previous observers, these organosols, excepting silver, are new; of those mentioned above, the copper and bismuth organosols were made by the second method, the others by the first one.

The organosols of sodium and potassium are very unstable; but the author has experimental ground for hoping to obtain more stable organosols of these metals.

It is of interest that the sodium organosols in ligroin, ligroin-naphthalene and ether are violet in color, while the corresponding potassium organosols are bluish violet. It is

known that cathode rays or Tesla currents act on the chlorides of sodium and potassium, turning them blue. Wiedemann[1] thinks that the blue color is caused by the formation of subchlorides. Elster and Geitel, however, believe the blue color to be due to solid colloidal solutions of the metals in their chlorides. The observed colors of the organosols would support the view of Elster and Geitel.

Svedberg considers this work preliminary and reserves the field. E. RENOUF.

The Stereoisomerism of Substituted Ammonium Compounds.

The preparation of stereoisomeric nitrogen derivatives has engaged the attention of a number of chemists during the past few years, and although, on the experimental side, a considerable degree of success has attended their labors, the theory of the subject has not, hitherto, been in a satisfactory state. An exception must be made in favor of the "syn" or "anti" compounds, of the type RR′C:NR″, such as unsymmetrical oximes, which are beyond the scope of this report.

The difficulties referred to arise from the fact that a few cases of isomeric compounds of the type $NR_3R'X$ (X = halogen) have been described, but no isomerides of the type $NR_2R'R''X$ could be prepared, except in the case of dicycloid compounds containing a nitrogen atom in each ring. The first example of this was observed by Aschan, it is doubtless due to the absence of free rotation. Compounds of the type NRR′R″R‴X have been repeatedly shown to exist in optically active forms and Wedekind[2] has examined a large number of such substances to determine the existence of spatial isomerides but, with the sole exception of the phenylbenzylmethylallylammonium salts, which he himself prepared,[3] all the derivatives of this type which previously had been regarded as stereoisomeric were found to differ in structure.

His conclusions in regard to phenylbenzylmethylallylammonium salts were confirmed, later, by Hantzsch and Horn.[4]

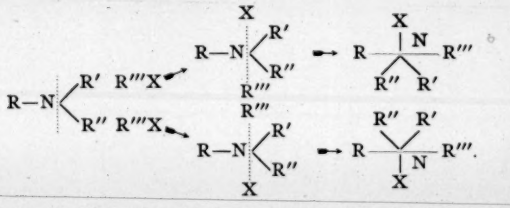
Some little time ago Le Bel showed[5] that the difference between compounds of the type $NR_3R'X$, which he had believed to be due to isomerism, in fact arose from isomorphism.

Kipping[6] proved that the salts of optically active acids and hydrindamine, which he had previously described, were not isomerides of the base, but were salts of isomeric acids. Hence,

[1] Wiedemann Ann., **64**, 78.
[2] Ber. d. chem. Ges., **30**, 178 (1902); **38**, 436 (1905).
[3] *Ibid.*, **32**, 517, 3561 (1899).
[4] *Ibid.*, **35**, 883 (1902).
[5] J. Chim. Phys., **2**, 340 (1904).
[6] J. Chem. Soc., **87**, 628 (1905).

it follows that no instance of spatial isomerism in an ammonium derivative has ever been observed except Wedekind's compound referred to above. In a recent paper[1] H. O. Jones records the results he has obtained by a reexamination of Wedekind's isomers. Neither compound can be transformed into the other. Unlike the β-compound the α-derivative is unsaturated, as is shown by the potassium permanganate test. The substances differ in other ways, including their action on methyl iodide, and on analysis it was found that the β-compound is really phenylbenzyldimethylammonium iodide, $C_6H_5N(CH_3)_2CH_2C_6H_5I$, while the α-derivative is the true phenylbenzylmethylallylammonium iodide, $C_6H_5NCH_3(CH_2C_6H_5)CH{:}CHCH_2I$. Thus the last instance of stereoisomeric ammonium derivatives is shown to be without existence in fact.

In the light of these observations Jones discusses the various suggestions which have been offered by Werner, van't Hoff, Willgerodt, Wedekind and Bischoff regarding the configuration of the ammonium derivatives, deciding in favor of Bischoff's "pyramidal" formula, with some simplification suggested by himself. He represents the formation of an ammonium salt from an amine, graphically, as follows:



The intermediate substance is regarded as being "a very unstable compound or as possibly only a state which arises when the amine and alkyl iodide first come within the sphere of each other's action." R‴ and X must be able to take up either of the two available valencies, because equal portions of *d*- and *l*-isomerides are always produced. The three groups in trivalent nitrogen compounds lie in the same plane as the nitrogen atom, during the change of valency the radicles group themselves into the most stable configuration, which is always the same for the same five radicles and is independent of the order in which they are introduced into the molecule. The author

[1] J. Chem. Soc., 87, 1721 (1905).

has written a highly interesting paper, and has materially contributed to the simplification of a troublesome and somewhat difficult subject.

J. BISHOP TINGLE.

REVIEWS.

HYPOCHLORITE UND ELECTRISCHE BLEICHE—Theoretischer Theil. By DR. EMIL ABEL. Monographien über angewandte Electrochemie. Band XVII. Halle a. S: Wilhelm Knapp. 1905. pp. 110. Price, M. 4.50.

Although almost a century has elapsed since Cruikshank first prepared sodium hypochlorite by the direct electrolysis of brine, the practical application of the idea has, for various reasons, never become an important factor in the bleaching industry. The reactions which obtain when an electric current is passed through a solution of common salt were found to be much more complicated than were formerly supposed, and, owing to the experimental difficulties involved in their study, the theory of the process has, until very recently, been little considered.

A very complete description of the various forms of apparatus which have been developed for the commercial production of bleaching liquor by direct electrolysis, appeared as Volume VIII of the series of monographs of which this work forms a part. Under the title, "Theorie der Hypochlorite," the author, some time ago, published a brochure in which he treated the subject at length, from a chemical point of view. In the present volume he has developed the process from the energy standpoint, giving the matter a purely thermodynamical treatment. He finds that, in this way, not only can the function of the electric current in the formation of hypochlorites be most easily determined, but that by thermodynamics alone can the true energy efficiency of the different technical methods for the preparation of hypochlorites be obtained.

The first part of the monograph is devoted to the calculation of the critical voltages of all the ions concerned in the reactions. A table giving the theoretical electromotive force necessary for the liberation of each ion of the first product is given.

The mechanism of the reactions taking place to form hypochlorite and also chlorate is discussed at length, the author giving great weight to the work of Foerster and his students on the theory of chlorate formation.

Those interested in the practical application of electrolysis for the production of bleaching liquor will find, however, the

last portion of the work of greater value than the first two-thirds, based as they are, on assumptions which, for the most part, are impossible of realization. In discussing the condition which must be observed in order that the maximum energy efficiency may be obtained, and the effect of the various additions to the brine which have from time to time been proposed, the author has rendered a distinct service to the electrochemist and engineer. W. H. W.

VERFLÜSSIGTES AMMONIAK ALS LÖSUNGSMITTEL. Materialien über die chemischen Eigenschaften des verflüssigten Ammoniakgases. Gesammelt von J. BRONN. Berlin: Julius Springer, 1905. pp. 251. Price, M. 6.

During the last forty years much work on liquid ammonia has been published, which Herr Bronn has collected and classified in this volume. While the author is especially interested in the technical uses of liquid ammonia as a solvent, the book will be of value to chemists generally. To indicate its scope, there are chapters on the properties of liquid ammonia; on the action of gaseous ammonia as a liquefier, with special reference to the work of Divers; on the absorption of ammonia by different substances; on liquid ammonia as a solvent; on metalammonium compounds and metalamids; on reactions and syntheses in ammonia solution; on reactions of the metalamids; and on physical-chemical work on liquid ammonia. E. R.

A TEXT-BOOK OF PHYSIOLOGICAL CHEMISTRY FOR STUDENTS OF MEDICINE. By JOHN H. LONG, M.S., Sc.D., Professor of Chemistry in The Northwestern University Medical School, Chicago. Illustrated. Philadelphia: P. Blakiston's Son & Co. 1905. pp. 424. Price, $2.50 net.

The writer has here presented a good elementary text-book of physiological chemistry for medical students. The style is clear and concise. The subject matter is divided into four sections as follows: The Nutritives; Ferments and Digestive Processes; The Chemistry of the Blood, the Tissues and Secretions of the Body; The End Products of Metabolism, Excretions, Energy Balance.

The directions for many experiments are inserted in the body of the text in fine print, so that the book will also serve as a laboratory manual for a brief course. Much of the recent work, such as Fischer's polypeptide investigations, is briefly presented by the author, and he also discusses in detail the tests of value to clinical medicine, such as the examination of stomach contents, faeces, etc., in consequence of which the pure physiological chemistry suffers considerable abridgment. A few inaccuracies of very minor importance have been noted.

Thus on p. 313 the statement is made that amyl salicylate is very readily hydrolyzed by liver extract whereas, compared with other esters, this one is really hydrolyzed by it very slowly indeed. On the whole the book is satisfactory and deserves to be recommended. A. S. L.

ELEKTROMAGNETISCHE SCHWINGUNGEN UND WELLEN. VON DR. JOSEF RITTER VON GEITLER. Braunschweig: Friedrich Vieweg und Sohn. 1905. Price, M. 4.50.

This volume on the subject of "Electro-Magnetic Vibrations and Waves" will not be of much interest to a student of chemistry, inasmuch as, up to this time, they have very few applications to chemical phenomena. To the physicist, however, the book is one of importance, and any one interested in the historical development of the subject will find it most profitable. The mathematical treatment is simple yet explicit; the description of experiments is clear and up to date, the references, specially to modern work, are most complete and the text is written in a lucid and attractive manner. Taken from every standpoint, therefore, the book is one to be recommended to all students of Philosophy, however advanced. J. S. A.

ANNUAL REPORTS OF THE PROGRESS OF CHEMISTRY FOR 1904. Issued by The Chemical Society. Vol. I. London: Guerney & Jackson. New York: D. Van Nostrand Co. 1905. Price, $2.00 net.

In this volume the English Chemical Society begins a series of annual reports on the progress of chemistry. The book covers the same field as Meyer's "Jahrbuch der Chemie" which has been published yearly since 1891. The "Jahrbuch" for 1903 contains 600 pages, the volume reviewed contains 280 pages. This is a distinct gain for the English journal, as such reports should be as brief in detail as possible. The table of contents shows that the different chapters are in competent hands: Chemistry, general and physical, James Walker; Inorganic, P. P. Bedson; Organic-aliphatic, H. J. H. Fenton; Organic-aromatic, J. B. Cohen; Stereo, W. J. Pope; Physiological, W. D. Halliburton; Agricultural, J. A. Voelcker; Mineralogical, A. Hutchinson; and Radioactivity, F. Soddy. E. R.

METHODS OF ORGANIC ANALYSIS. By HENRY C. SHERMAN, PH.D. New York: The Macmillan Company. 1905. Price, $1.75.

The purpose of this little work is to furnish students of organic chemistry with a convenient handbook for conducting the most common operations which they will be called upon to perform in the analysis of ordinary commercial products.

Chapter I. treats of the principles of ultimate and proximate

analysis. In the second chapter are given the standard methods for the determination of nitrogen, sulphur and phosphorus. The third chapter, on alcohols, is one of special interest at the present time, when chemists throughout the world are devoting so much attention to the analytical methods applied to beverages. The methods described mention all the prominent processes in the light of recent experience. The oxidation method for alcohols, comprising the substance known as fusel oil, has practically taken the place of Rouse's old process. The oxidation method gives fairly satisfactory results when applied to known quantities of the fusel oils. The statement by the author, therefore, that "neither method gives very satisfactory results" should be modified as applying only to the volumetric method. It has been found, also, that carbon tetrachloride is a better solvent for the fusel oils than chloroform. The author fails to mention this fact. The colorimetric method of determining the fusel oils is not referred to.

Chapter IV. deals with aldehydes; Chapter V. with the general methods for the carbohydrates; Chapters VI. and VII. with special methods. Chapter VIII. is devoted to the organic acids, especially to those of the aliphatic series. Chapter IX. treats of the general methods of examining oils, fats and waxes, and Chapter X. of the special methods for fatty oils. The salad oils are particularly mentioned in this chapter. Chapter XI. is devoted to butter; Chapter XII. to soaps and lubricants; Chapter XIII. to the proteids and cereals; and Chapter XIV. to milk. In the latter special attention is given to the preservatives which are used therein.

This book will prove useful to students and analysts in their work with foods and food products. H. W. W.